ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

HALLOYSITE IN INDUSTRIAL PAINT APPLICATIONS

M.Sc. THESIS

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Department of Polymer Science and Technology

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DECEMBER 2016

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HALLOYSİTLERİN ENDÜSTRİYEL BOYA UYGULAMALARI

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Melih Kamhi, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 515131034, successfully defended the thesis entitled "HALLOYSITE IN INDUSTRIAL PAINT APPLICATIONS", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

Played a major role in the emergence of this thesis, not sparing any time for help me and guiding me with her vast knowledge, I would like to endless thank to my thesis advisor Prof. Dr. Nurseli UYANIK.

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Melih KAMHİ
Chemist

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ABBREVIATIONS

TGA	**:** Thermal Gravimetric Analysis
PP	**:** Polypropylene
MF	**:** Melamine Formaldehyde
Eq	**:** Equivalent
SEM	**:** Scanning Electron Microscopy
GH	**:** Gardner-Holdt
KU	**:** Krebs Unit
HNTs	**:** Halloysite Nanotubes
DCOFA	**:** Dehydrated Castor Oil Fatty Acid
ASTM	**:** American Society for Testing and Materials
ISO	**:** International Organization for Standardization

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HALLOYSITE IN INDUSTRIAL PAINT APPLICATIONS

SUMMARY

Physics, chemistry, biology, electric/electronics, aviation and space technology, and medical sectors can be used nano materials and nano additives. Particulate, layered, tubular shaped nano materials are available in these fields.

Tubular structured halloysite is a natural mineral, cheap and effective additive. Due to this structure and large specific surface area, it uses in electronics, catalysis, biological systems, drug delivery, and polymeric composites provides the opportunity for advanced applications. The chemical formula of halloysite is $Al_4Si_4O_{10}(OH)_8.4H2O$. This high mechanical strength of nanomaterials, since they are used in conjunction with many polymers. Halloysite can be used without modification for some polymers, but sometimes it needs to be modified, depending of types of polymeric materials.

Paint is one of the newest important sectors where halloysite is used. Halloysite may be preferred to increase mechanical properties, corrosion and thermal resistance of paints. These nanomaterials can be mixed with many types of paint, due to empty lumen structure that can be used with corrosion inhibitor in anti-corrosive metal paints. Halloysite has effective flame retardant property owing to this, it is added to polymer to increase thermal resistance. Halloysite has similar characteristics with halogen based flame retardants on the other hand, it is compatible with nature.

In this study, halloysite was added to two types of curing and two different industrial paint formulation at different rates and many detail tests were applied to these paints to see the effects of halloysite. Firstly, epoxy ester resin was synthesized that was binder of paints then this resin turned into varnish with driers for testing. According to the results of these tests, synthesized epoxy ester had light color, quick drying, low hardness, high gloss, good adhesion and good impact resistance. Afterwards, the epoxy ester resin was used as a binder when two different paint formulations were prepared. These were air drying exhaust paint and oven curing metal paint. After paints were done these two different paints were separated equal to 5 gallons for the examine the effects of halloysite. First gallon did not contain any halloysite and respectively, 1%, 2%, 5% and 10% halloysite was added to 4 other gallons which were mixed at low rpm with a dispermat dissolver. Two different paint types for each of halloysite was added at low speed (500-600 rpm) even with all concentrations provided for easy compatibility, and could be mixed with paint. These paints have been subjected to detailed testing. These tests are viscosity, density, solid, covering properties, hardness (König), drying time, gloss, impact resistance, adhesion, flexibility and corrosion resistance. Outside of these tests, halloysite added paints were utilized TGA analysis for the interpretation of their thermal resistance. Halloysite did not effect in a significant way to that observed in the viscosity of the paint, just slightly increased the viscosity of the oven curing metal paint. Exhaust air drying paint had a very high density because of the high zinc content.

This density decreased with the increase of the amount of halloysite due to halloysite has a lower density than zinc. With the addition of halloysite increased the density of the oven curing metal paint. The consequences of coverage values were found to be quite high, halloysite did not have any negative effect on coverage values. Delaying the time of drying and curing of paint with the addition of this kind of additive is one of the undesirable features. It was observed that, halloysite did not have any effect on drying time and curing time of both paints. After came of the oven, cracks were seen on surface of metal paint. It was observed that cracks of surface gradually decreased with increased amount of halloysite. One of the most important results are gloss results for our study. According to these results, gloss results of oven curing metal paint showed an increase with the halloysite. Air drying paint had high hardness because it contained fairly high amounts of zinc content. The hardness of air drying paint decreased with halloysite which softened this paint. Oven curing paint had opposite situation. This paint showed lower hardness due to inorganic matter content and the hardness of paint increased when halloysite was added. Halloysite free air drying paint and oven curing paint showed excellent impact resistance and flexibility. It is found that halloysite did not any contribution to these properties. Adhesion tests were applied to four different surfaces. These surfaces are sheet iron, copper, galvanized, and aluminum. According to adhesion tests halloysite free metal paint had excellent adhesion to all surfaces and the paint did not cause any adverse effects to the addition of halloysite. Halloysite free air drying exhaust paint showed very good adhesion to entire surface, but the surface of aluminum has resulted in some reduction with increased amount of halloysite. Halloysite did not have negative effect on corrosion resistance of both curing paints. Moreover it was determined that corrosion resistance of air drying exhaust paint was quite high. TGA analysis yielded very important results. According to this analysis, the thermal resistances of paints enhanced against high temperatures and amount of mass loss was considerably reduced with the addition of halloysite.

HALLOYSİTLERİN ENDÜSTRİYEL BOYA UYGULAMALARI

ÖZET

Fizik, kimya, biyoloji, elektrik/elektronik, havacılık ve uzay endüstrisi ile sağlık sektörü nano malzemeler ve nano katkılar kullanmaktadır. Nano malzemeler, tanecik, tabakalı veya tüpsü yapıda olabilmektedir.

Tüpsü yapıdaki halloysit ise doğal bir mineral olup, ucuz ve etkili bir katkı maddesidir. Bosluklu boru şeklindeki yapısı ile büyük spesifik yüzey alanı sayesinde elektronik, kataliz, biyolojik sistemleri, ilaç taşıyıcı, emiciler ve fonksiyonel polimerik kompozit alanlarında gelişmiş uygulamalar için fırsatlar sağlar. Halloysitin kimyasal formülü ise $Al_4Si_4O_{10}(OH)_8.4H_2O$`dir. Bu nanomalzeme bazı polimerlerin çekme ve eğilmeye karşı dayanımını, termal direnç ve alev alma sıcaklığını, veya biyobozunmasını arttırmak için kullanılabilmektedir. Ayrıca polimerlerin sıvı ve gazlara karşı geçirgenliğini değiştirmek için de kullanılabilirler. Halloysitler bazı polimerlerle (poliamid, polietilen tereftalat, epoksi bazlı polimerler ve polisakkaritler) yüzey etkileşimi olmadan rahatlıkla karışabilmektedirler.

Halloysitin kullanılabildiği sektörlerden biri de boyadır. Bu sektörde halloysit, boyaların mekanik mukavemetini, korozyon ve termal direncini arttırmak için tercih edilebilirler. Bu nano malzemeler çok çeşit boyayla karışabilir ve bu boyaların mekanik mukavemetlerini oldukça arttırırlar. Ayrıca içerdiği boş tüpsü yapısı nedeniyle korozyon inhibitörleriyle birlikte antikorozif metal boyalarında kullanılabilirler. Halloysitlerin sahip olduğu en önemli özelliklerinden bir tanesi de etkili bir alev geciktirici olmaları nedeniyle, polimerlerin termal direncini arttırmalarıdır. Halojen bazlı alev geciktiricilerle benzer özelliklere sahip olmaları yanında, doğa ile uyumludurlar.

Bu çalışmada halloysitin farklı oranlarda iki farklı kürlenmeye ve formülasyona sahip endüstriyel boyalara eklenerek, kapsamlı boya testlerinin yapılması amaçlanmıştır. Bu boyaların bağlayıcısı olan epoksi ester reçine laboratuvar ortamında sentezlenmiştir. Epoksi ester reçinenin sentez aşamasında asit, viskozite ve solid değerleri takip edilmiştir. Sentez tamamlandıktan sonra bulunan asit, viskozite ve katı değerleri önceden belirlenen spesifikasyon değer aralıklarına girmektedir. Daha sonra sentezlenen bu reçineye kurutucular eklenerek vernik haline getirilip, bazı testleri boya yapımı öncesi kontrol edilmiştir. Bu testlerin sonuçlarına göre, sentezlenen epoksi ester reçine açık renkli, çabuk kuruyan, sertliği düşük, parlak, iyi derecede yapışma ve darbe dayanımı göstermiştir.

Daha sonra bağlayıcı olarak epoksi ester reçinenin kullanıldığı farklı iki boya formülasyonu hazırlanmıştır. Bu boyalardan bir tanesi hava kurumalı egzos boyası, diğeri ise fırın kürlenmeli metal boyasıdır. Bu iki farklı boya yapıldıktan sonra 5 eşit galona ayrılmış, 1 tanesi halloysit içermeyen olmak üzere diğer 4 galona sırasıyla %1, %2, %5 ve %10 halloysit eklenmiş, dispermat karıştırıcısı ile düşük devirde karıştırılmıştır.

Bu iki farklı boya yapıldıktan sonra 5 eşit galona ayrılmış, 1 tanesi halloysit içermeyen olmak üzere diğer 4 galona sırasıyla %1, %2, %5 ve %10 halloysit eklenmiş, dispermat karıştırıcısı ile düşük devirde karıştırılmıştır. Eklenen halloysit her iki farklı boya türü içinde, düşük devirde (500-600 rpm) dahi tüm konstrasyonlarda kolaylıkla uyumluluk sağlamış ve boyayla karışabilmiştir. Yapılan bu boyalar detaylı testlere tabi tutulmuştur. Bu testler; viskozite, yoğunluk, uçucu organik madde tayini (katı madde), örtücülük, sertlik (König), kuruma zamanı, parlaklık, darbe dayanımı, yapışma, esneklik ve korozyon direncidir. Bu testlerin dışında halloysit eklenen boyaların termal direncinin yorumlanabilmesi için TGA analizi yapılmıştır.

Boya testlerinin sonuçlarına göre, halloysitin boyaların viskozitelerine kayda değer bir biçimde etki etmediği gözlemlenmiş, sadece fırın kürlenmeli boyanın viskozitesini çok az arttırdığı görülmüştür. Hava kurumalı egzos boyası içeriğindeki yüksek çinko oranı nedeniyle oldukça yüksek yoğunluğa sahiptir. Farklı oranlarda eklenen halloysit ile birlikte bu yoğunluk, halloysitin çinkodan daha düşük yoğunluğa sahip olması nedeniyle düşmüştür. Fırın kürlenmeli metal boyasının yoğunluğu ise halloysitin eklenmesiyle birlikte yükselmiştir.

Her iki boya için de yüzeyleri kapatma sonuçları oldukça yüksek bulunmuş, halloysitin bu sonuçlara herhangi bir olumsuz etkisi olmamıştır. Bu tip katkıların boyaların kuruma ve kürlenme zamanını geciktirmesi istenmeyen özelliklerden birisidir. Halloysitin hava kurumalı boyanın kuruma zamanına herhangi bir etkisinin olmadığı, fırın kürlenmeli boyanın kürlenme zamanını ise geciktirmediği görülmüştür. Ayrıca yaklaşık yarım saat süre kürlenmesi için fırında bekletilen halloysit içermeyen fırın kürlenmeli metal boyasının film yüzeyinde çatlamalar olduğu görülmüştür. Halloysit eklenen boyaların ise halloysit miktarının artmasıyla birlikte, yüzeyde oluşan çatlaklarının giderek azaldığı görülmüştür.

Bulunan en önemli sonuçlardan bir tanesi de parlaklık sonuçlarıdır. Bu sonuçlara göre, halloysit eklenen fırın kürlenmeli metal boyasının parlaklığı oldukça artış göstermiştir. Hava kurumalı boya oldukça yüksek miktarda çinko içeriği nedeniyle yüksek König sertliğine sahiptir. Boyanın sertliği halloysit ile birlikte azalmış, halloysit boyayı yumuşatıcı etkide bulunmuştur. Fırın kürlenmeli boya için ise tam tersi bir durum söz konusudur. Bu boya daha düşük inorganik madde içeriği nedeniyle daha düşük sertlik göstermiş, halloysitin bu boyanın sertliğini arttırdığı gözlemlenmiştir. Darbe dayanımı testlerine göre iki farklı tip 10 boya da mükemmel dayanım göstermiştir. 80 cm yükseklikten boya yüzeylerine bırakılan ağırlığın bile, boya yüzeyinde direkt veya indirekt neredeyse hiç boya kaldırmadığı görülmüştür. Halloysitin boyaların darbe dayanımlarına herhangi bir etkisi bulunamamıştır. Haloysit içermeyen hava kürlenmeli ve fırın kürlenmeli boyaların esneklik sonuçlarının çok iyi oldukları tespit edilmiş, halloysitin bu sonuçlara olumlu veya olumsuz bir etkisi olmamıştır.

Boyaların yapışma testleri ise 4 farklı yüzeye uygulanmıştır. Bu yüzeyler; sac metal, bakır, galvaniz ve alüminyumdur. Testlerin sonuçlarına göre halloysit içermeyen fırın kürlenmeli metal boyası tüm yüzeylere mükemmel yapışma göstermiş, halloysitin eklenmesi bu boya için herhangi bir olumsuz etkiye neden olmamıştır. Halloysit içermeyen hava kurumalı boya da tüm yüzeylere oldukça iyi yapışma göstermiş fakat halloysit miktarının artması alüminyum yüzeyde bir miktar düşüşe neden olmuştur. Boyaların yüksek yapışma özelliğine sahip olması, 2 farklı boyanın da bağlayıcısı olan epoksi ester reçinenin yapışma özelliklerinden dolayıdır.

Boyaların korozyona karşı dirençlerini görebilmek adına, bu boyalar yaklaşık 500 saat tuz sprey cihazında bekletilmişlerdir. Cihazda bekletilen boyaların yüzeyleri görsel olarak incelenmiştir. Yapılan incelemelere göre, hava kurumalı boyanın boyanın korozyon direnci, fırın kürlenmeli boyaya göre daha yüksek bulunmuştur. Bunun nedeni içeriğinde yüksek miktarda bulunan çinkonun katodik koruma yaparak, zemini korozyona karşı korumasıdır. Halloysit eklenmesi boyaların korozyon direncine etki etmemiştir.

Son olarak yapılan TGA analizi cok önemli sonuçlar vermiştir. Bu analize göre hava kurumalı boya içeriğinde daha yüksek inorganik madde bulunması nedeniyle, fırın kürlenmeli boyaya göre yüksek termal dirence sahiptir. Halloysit eklenen boyaların ise kütle kayıplarının azaldığı ve termal dirençlerinin arttığı gözlemlenmiştir. Hava kurumalı halloysit içermeyen boyanın yaklaşık 800°C`de kütle kaybı %62.4, %10 halloysit içeren hava kurumalı boyanın kütle kaybı ise %33 civarındadır. Fırın kürlenmeli halloysit içermeyen boyanın kütle kaybı ise %68 bulunmuş, %10 halloysit eklenmesiyle bu oran % 65.4`e düşmüştür. Ayrıca bu boya için kütle kaybı için ilk kırılma noktası olan 240°C`nin 300°C`ye yükseldiği tespit edilmiştir.

1. INTRODUCTION

The phrases ‘paint’ and ‘surface coating’ are regularly used interchangeably. Surface coating is the more common description of any material that could be utilized as a thin continuous layer to a surface. Paints are usually used to explain pigmented substances as different from clear films which can be more properly known as lacquers or varnishes [1]. Paints can be classified various factors that are; basis of binder used, basis of properties or basis of application areas. According to binder types, oil paints, alkyd paints, latex paints, epoxy paints etc. are divided among themselves. Rust inhibiting paints, fire retardant paints, heat resistant paints or in tumuscent coatings are distinguished from each other, because they have different properties. Architectural paints, general industrial paints, marine paints, automotive paints, wood paints can be considered in according to the classification of application areas.

Due to higher expectation than other paints, nano materials began to be used in industrial paint groups. With reference to the advance of erosion and corrosion resistance, weathering and ultraviolet (UV-rays) resistance, water repellence and chemical resistance, dispersion stability and aging resistance, surface protecting and adhesion property, film smoothness and gloss retention along with different mechanical properties; nano materials adapted paints have shown in a number of industrial purposes. The purposes of suitable nanoparticles inside suitable ratio in paint formulations carry many advantages and opportunities to paint industries [2].

In our study, halloysite was used as a nano materials and its effects were investigated on the industrial paints. Halloysite is one of the natural clay minerals that contains kaolinite. Millions of years are required for the formation of this natural mineral from kaolinite. Halloysite chemical formula is $Al_2Si_2O_5(OH_4).2H_2O$ and under high temperature it can lose hydroxyl ions [3]. Natural halloysite is used as cheap nanocontainers with corrosion inhibitors into metal polymer coatings to provide sustained release. These corrosion inhibitors are benzotriazole, 2-mercaptobenzimidazole, and 2-mercaptobenzothiazole.

Halloysite added corrosion inhibitors at 5−20 wt % were used as additives for anticorrosive coatings. Polyurethane and acrylic coatings considerably improve their corrosion resistance with inhibitor loaded halloysite [4]. Halloysite can be added to epoxy as a impact modifier without scarifying flexural modulus, strength and thermal stability. Due to halloysite, impact resistance of epoxy increases nearly 400% [5]. Halloysite nanotube structure offers a flame retardant effect similar to that of halogen based flame retardants, except that the halloysite nanotubes are biocompatible in nature [6].

Owing to characteristics such as nanosized lumens, high L/D ratio, low hydroxyl group density on the surface, etc., an increasing number of interesting applications have been determined for these unique, reasonably priced and abundantly deposited clays [7]. Lately, halloysite began to be used in the paint industry. The investigations recommend that the nanocomposites exhibit markedly improved properties, such as advanced mechanical performance, a great deal better flame retardancy and thermal stability, increased corrosion resistance.

2. THEORETICAL PART

2.1 Epoxy Resin

Epoxy resins solely became commercially on the market about 1947. They show excellent resistance properties and it can be used in many applications. Polyamine, polyamide or polyamino-amide have functionality to create crosslinking structure with epoxy resin and it gives durable and resistant film. Epoxy resins are generally used for marine applications like ship's hulls, decks, superstructure and tanks, oil rigs and different off-shore installations, storage tanks for food, chemicals and water, pipe linings and paints for concrete and cement. The other using areas of epoxy resin are can linings or internal lacquers, automotive primers and powder coatings [8].

Epoxy resin coatings provide very good adhesion, chemical resistance, and physical properties that give outstanding protection against severe corrosive environments. These coatings are not used only to protect the metal of the container from corrosion, however additionally to protect the flavour of the contents, which may be affected by direct contact with metal [9].

Epoxy resins are usually not used alone however need a reaction partner so as to be cured (hardened). An oversized range of reaction partners is also used for solidifying at elevated or at temperature [10].

The epoxy resins most generally employed by so much in coatings are the bisphenol A primarily based epoxy resins, the generalized structure of that is given in Figure 2.1.

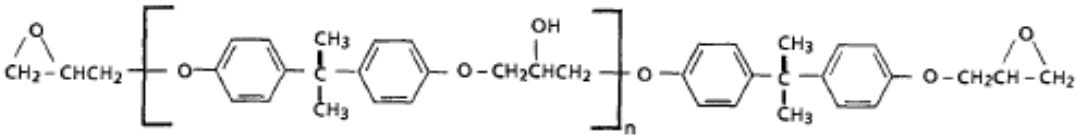


Figure 2.1 : Idealized structure of a bisphenol epoxy resin [9].

Epoxy resin coatings have wonderful mechanical strength and adhesion to several varieties of surfaces. Coatings notice applications in numerous paints, white ware,

automotive and naval sectors, for significant corrosion protection of every kinds. Epoxy coating formulations are on the market each as liquid and solid resins. Epoxy acrylic hybrid systems are available for household applications e.g., indoor and outdoor furniture and metal products. Environmental friendly coatings which is supported low priced epoxide resins are prepare from a natural nontoxic synthetic resin material like cardanol rather than standard phenol. Novolak resins are ready by the reaction of cardanol with gas and after epoxidized with epichlorohydrin [11]. These products were additional changed with diethanolamine in order that tertiary aminoalkane moieties are in the molecules that are required for self curing. Films from these epoxide resins are self-curable at 160 °C inside 30 minutes. The films exhibit good chemical resistance and they are often used as a primer coat and top coat on metallic substrates [12].

An intumescent coating has been designed employing a bisphenol A epoxy as binder. Expandable graphite, ammonium polyphosphate, melamine, and zinc borate create intumescent coating composition [13]. In solid lubricating coatings MoS_2-doped phenolic epoxy resin can be used. The friction and wear behaviors of the coatings were evaluated employing a ballon disk tribometer. Throughout the preparation, the materials were irradiated with oxygen, so friction coefficient increases and wear resistance decreases because of oxidative degradation of epoxy binder [15].

2.1.1 Epoxy ester

Terminal epoxide groups and the secondary hydroxy groups of solid epoxy resins can be reacted with fatty acids. It is called epoxy ester. Epoxy esters are prepared from fatty acid and epoxy resin in an inert atmosphere. Temperature must be between 240°C and 260°C [1]. Epoxy esters supply promising cheap renewable materials which used in several industrial applications as a result of they share many of the characteristics of standard petroleum based epoxy thermosets [16]. These resins contain vegetable oils so they are partly renewable materials. Due to the presence of functional groups, vegetable oils are comparatively converted into variety of functional derivatives [17,18].

Usually epoxy resin where n = 4 is used, and fatty acid content is chosen for esterify between 40% and 80% of the available groups including hydroxyl. Air-drying brushing finishes produced from medium (50 - 70% modified) and long (over 70%)

oil epoxy esters of drying oil fatty acids. Short (30-50%) oil-drying or non-drying fatty acid esters are utilized in industrial stoving primers and finishes. Epoxy ester resin which is stoved has excellent adhesion, flexibility and chemical resistance like alkyd / MF formulations. High aliphatic solubility, better exterior durability, decreased hardness, gloss, and chemical resistance are related to increased fatty acid content [1].

During the synthesis of epoxy esters, solid, acid and viscosity values are checked over time. Specification value ranges for amount of solid, acid value and viscosity values are determined before the synthesis step. The amount of solid is given as a percentage and acid value is given as a mg KOH/g for epoxy ester. Viscosity of epoxy ester is controlled as a Gardner-Holdt value. The Gardner-Holdt viscosity is given in seconds and the corresponding unit is written. Gardner-Holdt seconds values are given in the following table (Table 2.1) of the Gardner-Holdt unit and poise counterparts.

Table 2.1 : Gardner-Holdt viscosity conversion chart.

Gardner-Holdt Second	Gardner-Holdt Unit	Poise	Centistokes
1.46	D	1.0	100
2.93	H	2.0	200
4.4	L	3.0	300
5.8	P	4.0	400
7.3	S	5.0	500
11.6	U – V	8.0	800
18.9	X	12.0	1200
25.8	Y	17.6	1760
33.3	Z	22.7	2270
39.6	Z1	27.0	2700
49.85	Z2	34.0	3400
67.9	Z3	46.3	4630
91.0	Z4	62.0	6200
144.5	Z5	98.5	9850

2.1.2 Vegetable oils in coatings and paints

Vegetable oil species and its varieties produce oils with different properties attributable to their composition. These oils according to their major fatty acid composition can be classified into laurics and oleics. Some natural oils can easily polymerize with atmospheric oxygen. These oils known as drying oil. Traditionally drying oils are crucial raw material for industrial paints and coatings. Drying oils are extremely unsaturated oleics. They contain high percentage of linoleic and linolenic

acids, or conjugated fatty acids. Drying oils form a tough, elastic, waterproof film which adheres firmly to surface when subject to air in a thin layer. Nondrying oils are separated by their ingredient of saturated fatty acid or fatty acid which contains only one double bonds (e.g., oleic acid). They do not pronto take up oxygen to create cured films. The other group of oils are semidrying oils. When they subject to air in a thin layer, they can be thickening but cannot create hard and dry film [19].

Vegetable oils preponderantly accommodates triglyceride, the glycerin esters of fatty acids. Fatty acids are obtained jointly of the chemical reaction product of triglycerides with 5 major styles of fatty acids of chain lengths starting from sixteen to eighteen carbons with zero to three double bonds: palmitic, stearic, oleic, linoleic and linolenic acids (Figure 2.2) [20].

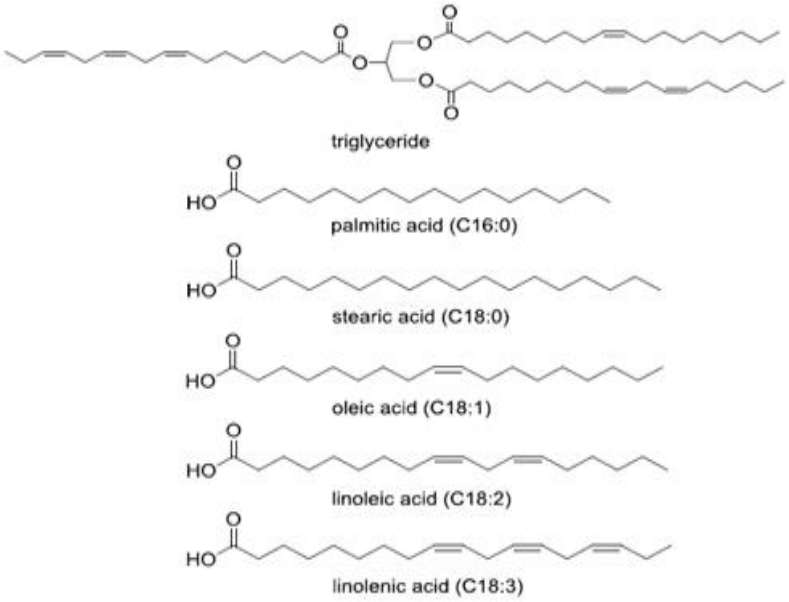


Figure 2.2 : Structures of triglyceride and five most important fatty acids [20].

Vegetable oils found application in air drying paints, varnishes and different coating processes that start to the times of cave paintings (ca. 30.000 yr ago) [20]. Alkyd resin (i.e., alcohol acid) traditionally among the oldest polymers derived from vegetable oils and they are wide utilized in a spread of economic coating applications. They are ready by the transesterification of polyols with polyacids / anhydride and vegetable oils / fatty acids [8].

In industry epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) are now only bio-renewable epoxies [8]. Epoxidized vegetable oils are often prepared by the epoxidation of the double bond of fatty acids using peracids and such processes have

been used since the 1940s [21,22]. Application of the epoxidized vegetable oil has been actively widened. Various thermosetting polymers are synthesized from epoxidized vegetable oils through properly selecting curing agents or curing conditions, through new formulation approaches in composites, coatings and toughening agents unit of measurement being incessantly developed. However most significant, new epoxy monomers derived from vegetable oils are with success synthesized that show additional promise than common epoxidized vegetable oil in terms of reactivity and thermal and mechanical strength. The new monomers are powerful step towards advanced applications, like structural composites, created possible through improved structure, reactivity and correct alternative of formulation conditions [20].

2.2 Halloysite

Halloysite was first delineate by Berthier (1826) as a dioctahedral 1:1 clay mineral of the kaolin group. According to Churchman (2000), halloysite happens wide in each weather beaten rocks and soils and it has been known as having shaped by the alteration of a good type of styles of each igneous and non igneous rocks. However, halloysite usually forms a main part of andisols and soils derived from volcanic materials in wet tropical and semitropic regions [23]. The structure and chemical composition of halloysite is analogous to that of kaolinite, dickite or nacrite however the unit layers in halloysite are separated by a monolayer of water molecules [24]. In early years it was absolutely tough to differentiate halloysite from different minerals, significantly from mineral. However, X-ray analysis has shown that it is distinctive crystalline structure [25].

Halloysite has been extensively used as a material for ceramics, particularly for the manufacture of ceramic ware, and bone china [3,26]. Having nanotubular structure, halloysite particles probably applied in many fields of nanotechnology [27,28]. These multilayer tubes are usually used for plastic composites, in controlled release applications, and can be coated with metal by electroless plating to form conductive fillers [29].

Halloysite happens in nature as a hydrous mineral consisting from rolled alumosilicate sheets that has the unique formula of $Al_2Si_2O_5(OH)_4.nH_2O$, that is analogous to mineral apart from the presence of an extra water monolayer between

the adjacent layers. When n = 2 the mineral is named halloysite, –10 Å attributable to its layer periodicity of 10 Å. Heating halloysite –10 Å irreversibly dehydrates it to halloysite –7 Å with n=0. Dehydrated halloysite features a formula of $Al_2Si_2O_5(OH)_4$ with layer spacing of concerning 7.2 Å [3,30].

Pure halloysite could be a white mineral and may simply be processed to get fine powder (Figure 2.3). However, in some cases the mineral is colored from yellow to brown and typically green looking on the deposit. The rationale for these colors are trace amounts of the metal ions like Fe^{+3}, Cr^{+3}, Ti^{+4}, etc [3] that substitute Al^{+3} or Si^{+4} within the halloysite mineral. SEM pictures of the halloysite samples clearly indicate that they show hollow nature.

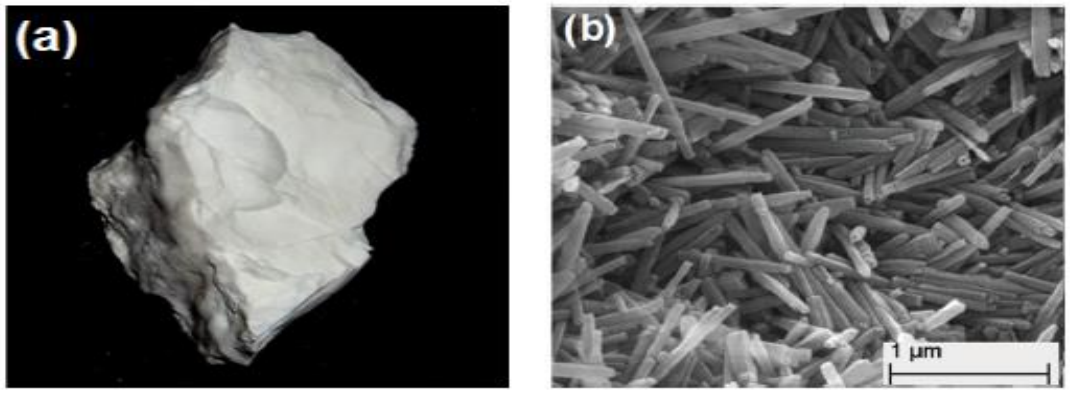


Figure 2.3 : a) Raw halloysite mineral, (b) SEM image from the rock, showing over 99% nanotube content [3].

Halloysite layer consists of the bilayers of aluminum and silicon oxides (Figure 2.3 a). Dimensions of the halloysite tubes vary depending on deposit, i.e. each deposit has halloysite with certain diameter and length. Overall, the outside diameter of the tubes varies from 50 to 200 nm, and therefore the diameter of the interior lumen ranges from 10 to 40 nm [21]. The lengths of the tubules are within the vary 0.5 – 1.5 µm [28,31,32].

One of the specialties of the halloysite is that the totally different surface chemical properties at the inner and outer sides of the tubes (Figure 2.4 a) [33,34]. The silicon oxide layer has relevancy to the outer surface of tube, whereas the aluminium oxide layer has relevancy to the inner lumen surface. Aluminum oxides and silicon oxides have totally different dielectric and ionization properties, that is clear from the observations of electrical zeta-potentials of those chemical compound nanocolloids in water. The primary one (alumina) has electric charge up to the pH value of the

solution 8.5, whereas the opposite one (silica) is negative on top of pH 1.5 (Figure 2.4 b). The power to possess totally different charges at the inner and outer components of the halloysite nanotubes permits for the selective loading of charged molecules within the nanotubes [27,28].

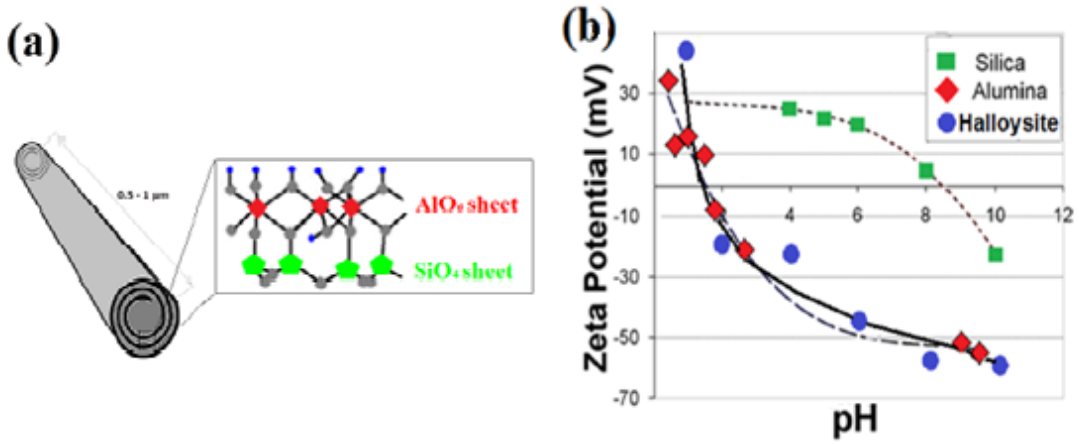


Figure 2.4 : a) Schematic representation of the halloysite tubular structure and wall chemistry, (b) variation of the silica and alumina surface potentials by pH of the solution [35].

Many countries, like China, France, Belgium and New Zealand, have deposits of natural HNTs. In contrast to different tubular materials (such as boron nitride, metal oxide (MO), and carbon nanotubes), halloysite is generously available natural nanomaterial, that makes it engaging and convenient for technological applications. Halloysite based nanocomposites are studied for many decades owing to their chemistry properties, as well as their tubular structures, ion exchange, and hydrophobicity [36].

2.2.1 Applications of halloysite

Elongated tubular shape with lumen halloysite can be used as a nanocontainer, and being environmentally friendly, halloysite mineral may be extensively utilized in the industry. Unlike alternative nano-tubular materials (such as boron nitride, silica or carbon nanotubes) halloysite may be a pronto obtainable low cost material, that makes it enticing for several technological applications. It belongs to the family of the clay minerals and may substitute kaolinite, montmorillonite, and bentonite as additives in composites. Significantly in paper production, modification of wood fibers by halloysite nanotubes were proved to extend the brightness and porosity of

the paper sheets [37,38]. Halloysite can be used in polymer composites and paints with many applications.

2.2.1.1 Polymer composites

Polymer clay nanocomposites enable enlarged tensile and flexural strength [39]. improved thermal resistance and flame retardancy [40,41] reduced gas and liquid permeability and enlarged biodegradability [39]. Two most ordinarily used fillers for polymer nanocomposites are platy clays such as montmorillonite, hectorite and saponite [39], and carbon based fillers such as carbon fibers, nanotubes and graphene [42,43]. Halloysite nanotubes have some advantages over carbon primarily based fillers: they are naturally available, less expensive than carbon nanotubes. Furthermore, they are not toxic. Halloysite nanotubes are less tough than carbon nanotubes, but they still offer important improvement in polymer tensile strength (5-10 wt fine addition typically doubles the composite strength) [42,43]. Halloysite even have sure blessings over platy clay minerals. Platy clay sheets are powerfully stacked to each other which needs tough and costly exfoliation method to get smart dispersion inside polymer matrix [39].

Halloysite has considerably less surface hydroxyl groups, capable of forming hydrogen bonded stacks or aggregates, and its tube form prevents tight particle stacking. Halloysite can easily dispersed in several polymers with none surface treatments (e.g., polyamides, polyethylene tereftalates, epoxy based polymers, and polysaccharides) [7].

Polypropylene is a vital thermoplastic polymer employed in a spread of applications including cable, film, pipe, and container attributable to high resistance to several chemical solvents, bases and acids. However, low strength, low softening point, and flammability limit its wide application. At the same time, it is necessary to switch polypropene to urge improved mechanical properties, flame retardancy also thermal stability. Incorporation of 5% halloysite in polypropylene considerably enhanced the flexural modulus on 35% whereas tensile strength was improved by 6.1%. Silanization of halloysite not solely expedited the dispersion of halloysite in polymer matrix however conjointly increased the surface bonding, therefore additional rising the mechanical strength of polypropene [6].

Thermal stability and flame retardation result of the polymer may even be improved

by incorporation of halloysite. Soft blending of halloysite and polypropylene resulted in increased thermal stability and reduced flammability of halloysite / polypropylene, that attributed to the halloysite barriers in heat and mass transport yet because the presence of iron in halloysite [40]. The thermal insulation barrier at their surface throughout burning may either retard the burning while not stop or additional typically double the overall burning time [44].

Halloysite will increase the fracture toughness, strength and modulus of epoxy while not losing their thermal properties. Combination halloysite with epoxy severe shear stresses could cut up the agglomerates to realize a uniform dispersion, that can not be eliminated by applying standard mechanical mixing (ultrasonic vibration or magnetic stirring) [44]. Incontestable that ball mill homogenisation and potassium acetate treatment were effective approaches to decrease the size of halloysite particle within the epoxy matrix [45]. The constant of thermal expansion of the epoxy was considerably reduced and also the modulus of the epoxy within the glassy state and rubbery state were considerably increased by the addition of a little quantity of halloysite compared with the cured resin [46].

Rubber is employed extensively in several applications either alone or together with different materials. The strengthening of rubbers by particulate materials like carbon black and silica has been extensively studied. Rubber / layered clay shows excellent mechanical properties moreover lower permeability [44].

Utilized both mechanical and solution mixing method when prepare halloysite / natural rubber nanocomposite these mixing methods can be increased scorch time, cure time and maximum torque. Solution mixing method is more effective method rather than the mechanical mixing method because it shows higher tensile strength, tensile modulus, fatigue life and decomposition temperature at a lower percentage of weight loss [47]. Addition of halloysite into styrene-butadiene rubber supported the dispersion and orientation of halloysite nanotubes in polymer matrix and reinforced the surface interactions via hydrogen bonding and valency bonding, and therefore leading to accumulated the mechanical properties of nanocomposites like hardness and modulus [48].

Halloysite nanotubes are effectively used as nucleating agents for many polymers like polyethylene, isotactic polypropylene [49,50], butene terephthalate [51] and

polyamide 6 [52]. Unlike alternative clay fillers halloysite does not need organic surface modifiers like quarternary amine salts or organosilanes that lower the surface energy. The surface energy is believed to be accountable for the formation of crystalline spherulites as shown in Figure 2.5. Addition of 30% halloysite in isotactic polypropylene at 20ºC/min cooling rate non isothermal peak temperature of crystallization was increased from 110.7 to 119.6 ºC while crystallization half time reduced from 0.525 to 0.458 min. Activation energy of crystallization accrued from 206.2 to 267.3 kJ/moles, that is related to confinement effect of halloysite which is restricting polymer chain movements [50]. It has been reported that polyamide 6 and polybutylene terephthalate composites showed similar effects [51,52]. Conversely organo modified montmorrilionite did not show any crystal nucleation because of the reduction of surface energy by surface treatment [51].

Nucleation capability together with fine dispersion, higher nanotube tensile strength and interaction with polymer chains is believed to be main reason behind tensile and impact strength improvement, whereas increased nucleation additionally considerably reduces the cycle time for extruded extruded polymer parts [53].

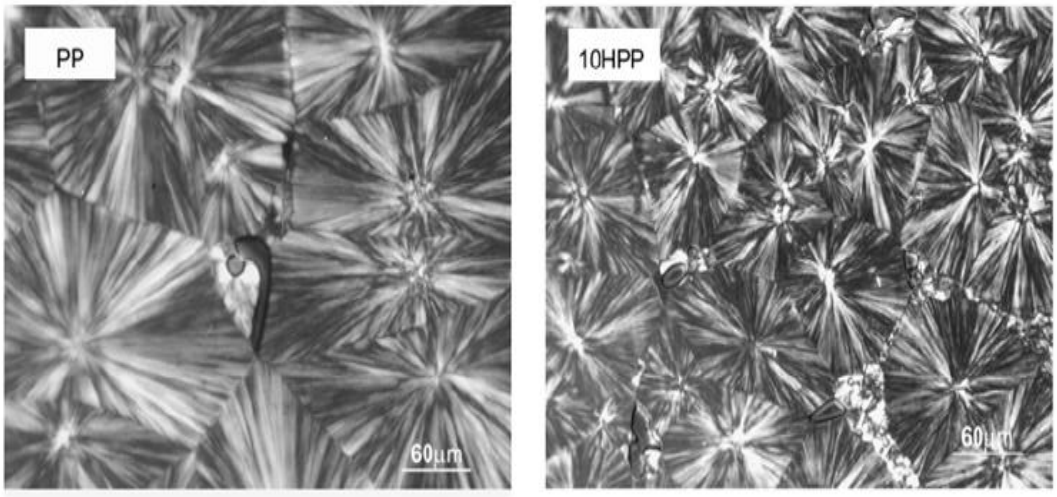


Figure 2.5 : The final crystal morphology of pure polypropylene and polypropylene 10% halloysite composites crystallized at 128°C [49].

Halloysite modified polymer composites has higher thermal stability and flame retardancy rather than neat polymers. Addition of approximately 10% halloysite enhanced maximum weight loss temperature of polypropylene from 351°C to 425 °C. 10% halloysite-PP composite generated double less smoke compared to neat polymer and needed 50% more time for ignition according to cone calorimetric

analysis [54]. Halloysite-polyamide [55] and halloysite-epoxy [56] nanocomposites showed similar affects.

2.2.1.2 Coatings

Another halloysite using area is paint industry. Paint products contain many nanoparticles like titanium dioxide (rutile), silica, clay, mica, latex, etc. Some of these nanoparticles enhance the properties of the paint whereas others are used only for the reduction of the product value [1,57]. Halloysite particles easily miscible with diversity of the coatings and especially enhance their mechanical properties [53].

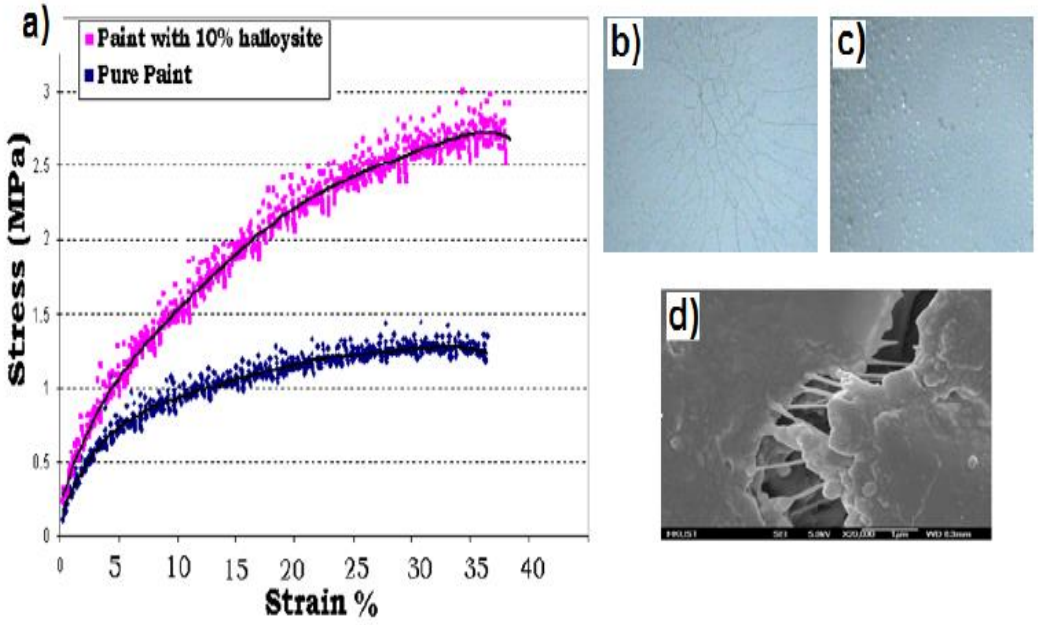


Figure 2.6 : Mechanical properties of pure paint and halloysite paint nanocomposite: (a) stress-strain relationship, and images of the (b) pure alkyd paint and (c) paint with 10% halloysite after rapid deformation test, (d) SEM image of microcrack on halloysite epoxy composite coating [5].

In Figure 2.6 a, stress-strain relationship of the blue paint without halloysite and halloysite paint composite is shown. Tensile properties of the paint increase due to addition of 10% halloysite. Moreover halloysite paint shows much better performance against rapid deformation as compared to pure paint as demonstrated in Figure 2.6 (b) and (c). A 0.2 kilogram metal bar was dropped to the painted metal plate from the height of 1 m in order to subject plates to the rapid deformations and metal plates thickness was 1 mm. Metal coated with pure paint has a lot of cracks on its surface because of the rapid deformation, on the other hand the same paint containing 10% halloysite did not show any cracking [57]. This is remarked

dissipation of the impact energy by halloysite pull out and prevented crack propagation due to bridging of microcracks [5].

Corrosion inhibitors with halloysite can be loaded to gain sustained slow release. Being suitable with polymer paints, loaded halloysite tubes are without difficulty miscible with metal coatings. Earlier it was recounted that addition of 10% halloysite into paints vastly improves their tensile properties. Moreover to all these benefits, because of its empty lumen, halloysite nanotubes can be applied to entrap corrosion inhibitors, which can also improve anticorrosive steel coatings [58,59].

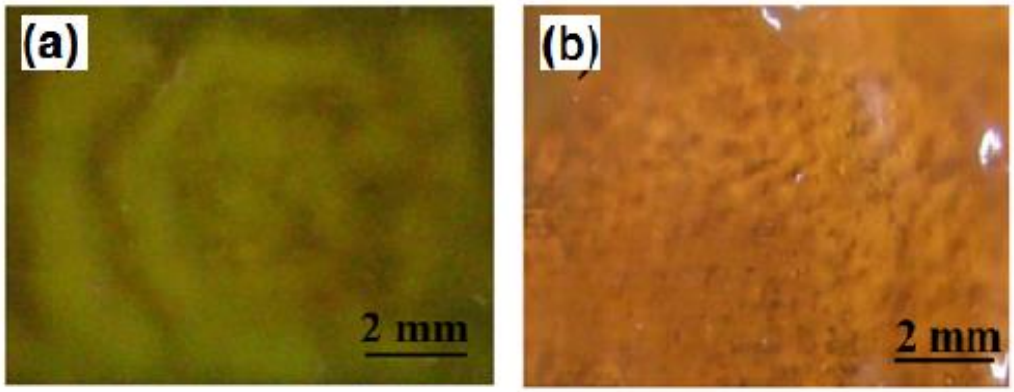


Figure 2.7 : Copper strips coated with (a) pure paint and (b) paint-halloysite nanocomposite [60].

Corrosion resistance take a look at on the painted copper strips (Figure 2.7) revealed the expanded corrosion inhibition performance of the coatings on the basis of the paint-halloysite composites. Strips were exposed to particularly corrosive liquid containing 30 g/L of NaCl, for 6 months. As it is visible from the image big quantity of green corrosion products had been accumulated beneath the paint on strips coated with ordinary paint even as strip covered with halloysite-paint composite indicates no proof of corrosion [60]. The cause for the increased corrosion resistance of this coating is the slow release of the corrosion inhibitor entrapped into the hollow lumen of the tubes. Corrosion inhibitor slowly releases to the corrosive media as soon as the paint is damaged causing the recovery of the damage. Halloysite nanotubes additionally substantially improved the anticorrosive performance of the sol-gel coatings. Shchukin showed that tubules loaded with numerous natural corrosion inhibitors consisting of benzotriazole and 8-hydroxyquinoline vastly improves the anticorrosion property of the coatings for aluminum [59,61,62].

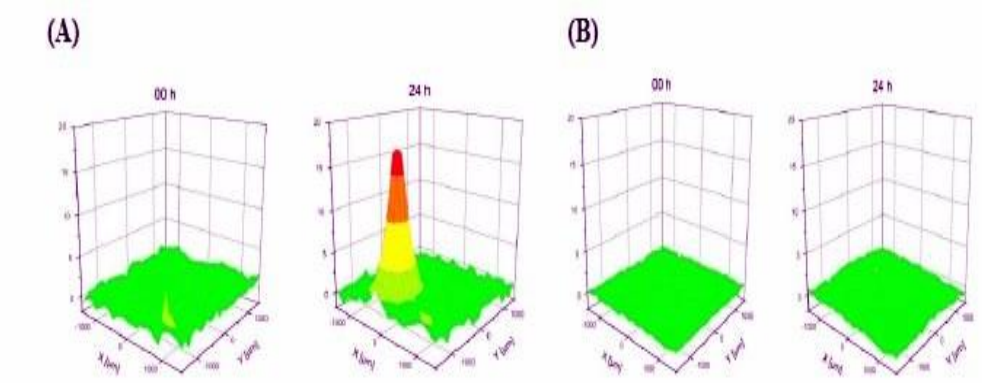


Figure 2.8 : Current density measurements using the scanning vibrating electrode technique. Metal strips made from aluminum which were coated with usual solgel coating (A), and with sol-gel containing halloysite (B) [62].

In Figure 2.8, localized corrosion current densities on coated and artificially scratched metallic strips are shown. Corrosion current densities had been measured by using the use of scanning vibrating electrode technique, a process that makes use of vibrating PtIr electrode to detect corrosion current densities at specified areas of metal surface. The activity of the anodic corrosion current at the scratch of the pure sol-gel film was very high and swiftly increased throughout a couple of hours, which is the indication of fast corrosion process. However, within the case of modified sol-gel coating with halloysite nanotubes corrosion system used to be significantly decreased. No corrosion present was detected over 24 hours and this evidently indicates that incorporation of inhibitor loaded halloysite tubes into sol-gel coating drastically reduced the rate of corrosion process [59,62].

2.3 Industrial Paint

To the paint industry ‘industrial paints’ are the ones coatings utilized by industry at huge, as opposed to painters and interior designers, painting contractors, and do-it-yourselfers. General industrial paints include wire enamels, clear and pigmented furnishings finishes, can lacquers, tractor finishes, paints for toys, plane finishes, paper coatings, domestic equipment finishes, safety for automobile components, coatings for plastics, and so on. Industrial materials can be as large as roadgrading machines or as small as dice. They are are regularly made of steel, however can also frequently be product of wood, wood composites, paper, card, cement products, glass, or plastic. Metals can be steel in any of its forms, with or without protective surfacing, like galvanizing or tin, or they can be aluminium, zinc, copper, or any of

the severa alloys. Each substrate and end use is an another paint trouble, which have to be solved within the commercial and other constraints of factory processes. There is therefore no such issue as a normal preferred general industrial paint or painting. Most sub-classifications of general industrial paints are established upon the industries served with those paints, e.g. drum paints for the steel and plastic drum industry. These classifications are frequently utilized in statistical records on paint utilization. Tables 2.2-2.3 illustrating the volumes of paint used and the commercial markets served inside the UK and other [1].

Table 2.2 : The UK market for industrial finishes (1994) [1].

Industrial market	**Volume, litres ($x10^6$)**	**%**
Agricultural, construction and earth-moving equipment	6	4.7
Auto components	2	1.6
Aviation	4	3.1
Can	19	14.9
Coil	12	9.4
Domestic appliance	2	1.6
Drum	3	2.3
Electrophoretic	4	3.1
Furniture	11	8.6
General machinery	10	7.8
Joinery	2	1.6
Metal fabrication	14	10.9
Paper	4	3.1
Plastics	5	3.9
Powder (allowing 1.5-1 kg^{-1})	30	23.4
Total	**128**	**100**

Table 2.3 : West and Central European market for industrial finishes (1992) [1].

Industrial market	**Volume, tonnes ($x10^3$)**	**%**
Agricultural, construction and earth-moving equipment	90	4.7
Aviation	25	1.3
Can	155	8.1
Coil	100	5.2
Domestic appliance	180	9.4
General industrial uses	650	33.9
Plastics	45	2.3
Powder	160	8.3
Wood finishes	320	16.7
All others	195	10.1
Total	**1920**	**100**

Industrial paints are subjected to various tests after they are made. The manufacturer always have the same physical and chemical properties to produce the paint, the paint of the consumer that the job will use physical and chemical in order to choose and to know the properties is required. Some of the test methods applied to the paints are; viscosity, density, solid, covering properties, gloss, hardness (König), drying time, impact resistance, adhesion, flexibility and corrosion resistance.

The paint viscosity is an important feature that comes to mind first, and always is a value that is specified in the specification. For this reason, it is necessary to ensure that this characteristic of the paint (viscosity, flow, consistency) is appropriately used for the purpose of painting. It is also important that the viscosity of the paint also affects properties such as spreadability, sagging, flow, brushability or sprayability which are functional during application. Many tools have been developed to measure other paint properties associated with viscosity and viscosity along with developing paint technology. One of the most frequently used viscosity units in the painting is the Krebs Unit. In the Table 2.4 can be find the conversion of Krebs Unit according to other units.

Table 2.4 : Krebs Unit viscosity conversion chart.

Krebs Unit	Poise	Centistokes
30	0.50	50
33	0.60	60
37	0.80	80
40	1.0	100
52	2.0	200
60	3.0	300
64	4.0	400
68	5.0	500
71	6.0	600
85	10.0	1000
103	20.0	2000
121	30.0	3000
133	40.0	4000

The density of paint shows the relationship between weight and volume, it may be necessary for the calculation of paint consumption. However, selection of the formulation and packaging of the paint (size and type), finished densities of the paint are important. The density of the paint is given as a g/cm^3 or g/ml under a certain temperature.

The amount of solids in the paint is the ratio of the amount of binder, pigment and filler in paint to the total amount of paint. For each paint, there are at least two solids are found and the average the value of solids is given in % by weight.

The covering value of the paints can be defined as the power to completely cover the surface to which it is applied. As it is known, the covering ability comes from the pigment contained in the paints. The value of coverage can be find as % by UV spectrophotometer.

Dry paint film is described as the paint film thickness resistance to external physical and atmospheric conditions. The hardness of the paint is commonly measured as pendulum or pencil hardness. Pendulum hardness is given by König.

In oven curing paints the drying time is already determined. The painted part should be kept at a certain temperature for a certain period of time. The drying of air drying paints is a fairly long process in which the various stages can be expressed in different terms that have the same meaning or are very close to each other. These commonly used terms are powder drying, touch dry, full dry, retouchability, sanding time.

The paint shows resistance against the sudden forces applied on the dry film which is

called impact resistance. This test is made with special impact devices made for paint. The maximum height at which a dry paint film shows resistance is expressed in inches or centimeters.

Adhesion is the case where the paint is held together with the applied surface. Chemical and / or physical forces are responsible for keeping the surfaces together. Dry paint removal from the surface of the film in different ways because of different measurement methods are applied. Cross-cut test is the most important adhesion test of paint. Its evaluation criterions are; Gt-0 (excellent), Gt-1 (very good), Gt-2 (good), Gt-3 (medium), Gt-4 (poor).

Paint gloss refers to the reflection of light falling on a surface, the degree of sharpness of the image formed on the surface by rays from a source. The gloss depends on the pigment / binder ratio of the paint, the amount of fillers in it, whether grinding step in the paint production is done at a sufficient level. Light source with 20^o, 60^o, 85^o angles dropped to surface and the values are noted.

Elasticity for paint type materials is defined as the ability to bend and stretch the paint film without any failure. The dry film elasticity of the paint is examined by severe tests. Thus, the resistance against the deformations that the paint will be subjected to later will be pre-tested. For measuring elasticity, one or all of conical bending, cylindrical bending and deep drawing devices can be used. Conical bending test is the most common elasticity test applied to industrial paints. After the conical bending test is performed, evaluation is made as "pass" or "fail".

The most important test done to see the corrosion resistance of paint is salt test. This test is a test developed specifically to measure the performance of paint systems to prevent corrosion. Usually, rust propagation from the scratch, rust on the panel surface, bubbling in the paint film, cracking, etc., are noted and evaluated in the form of comparison or evaluation.

2.3.1 Metal Paints

The utility of metal coatings for the protection of metals can be required for one or extra of the following motives:

(a) to save you or lessen corrosion of the substrate metal

(b) to alter the physical or mechanical properties of the substrate steel

(c) to create and hold a few desired decorative impact

Many coatings actually have a position in wear resistance and may have other essential properties to be considered, for instance, silver electrodeposits for electrical contacts. Despite the fact that the initial choice of coating material applied for reasons (b) or (c) can be dictated through the particular properties required, the corrosion behavior of the composite metal coating–metal substrate system have to also be taken into consideration in so far as it may additionally have an effect on the maintenance of the desired properties. Consequently, in all instances wherein shielding metal coatings are used, the corrosion overall performance of both coating and substrate requires careful consideration [63].

Metallic dusting depends on the potential of the material to increase a protective oxide scale. Lots of the conventional low cost steels extensively used in plant technology do not own a enough capacity for shielding oxide scale formation. On the other hand, with a purpose to prevent corrosion of the substances, protective coatings rich in Al, Cr, Ti and Si can be applied that may form protective oxide scales and, hence, protect the underlying substrate from corrosive assault. Al, Cr, Si and Ti produce diffusion and overlay coatings for motives in their capability to shape very solid protecting oxide layers [64].

The particular features of those elements in a coating system are:

Al: Formation of protecting thermodynamically very stable Al_2O_3 or with chromium (Al,Cr)-oxide [64].

Si: Formation of protecting thermodynamically very strong SiO_2. Si furthermore can enhance ductility of coatings [65].

Ti: Promotes (in aggregate with Al) the formation of Al_2O_3 at low temperatures. Formation of protecting thermodynamically very stable Ti-oxides [64].

Cr: Acts as inter-diffusion barrier for Al and forms Cr_2O_3 [64].

Previously already several coatings had been utilized to distinctive materials with a view to guard them towards metallic dusting attack [66,67,68]. Consequently, the oxide scale shaped on such coatings should be homogeneous, adherent and free of pores and defects [69].

2.4 Literature Survey

2.4.1 Halloysite nanotubes as a anticorrosive agents in paint

Some of the important utility of halloysite nanotubes is its use as a nanocontainer for anticorrosive agents. Abdullayev et al. showed that after the halloysite nanotubes are loaded with benzotriazole and admixed with an industrial paint, it drastically improves the anticorrosive properties of the paint. Halloysite nanotubes have a loading effectiveness 4.5% of the weight of halloysite, when loading is carried out in acetone. Halloysite nanotubes loaded with benzotriazole are compared with the sol-gel based coatings to determine surface protective activity. The samples are subjected to the corrosive atmosphere for 24 hours to measure the anodic corrosion activity. It is determined that anodic corrosion on the sol-gel established coatings raises quickly in a number of hours, leading to a pitting variety of corrosion [59].

When the halloysite nanotubes mixed acrylic paint coated on copper metal wire is exposed to a corrosive atmosphere, the concentration of Cu^{2+} ions corroded is significantly lowered than the controlled sample [58].

Together with benzotriazole, other anticorrosive agents like 2-mercaptobenzothiazole (2-MBT) and 2-mercaptobenzimidazole (2-MBI) are also effectively loaded into halloysite [33,70].

2.4.2 Halloysite nanotubes for increase mechanical properties of paint

The pencil hardness of a two-component polyurethane coating was increased by halloysite nanotubes loading which was less than 10% wt. The pencil hardness used to be round F for the unfilled coating and expanded to round 2H upon filling. This finding can also be rationalized through HNTs forming a mechanical network throughout the polymer matrix because of their elongated form. SEM micrographs showed that the nanotubes have been all good immersed within the bulk of the film. The films were optically transparent. Applications will undoubtedly be in areas the place hardness wishes to be completed in mixture with different, probably conflicting, engineering targets [71].

2.4.3 Halloysite nanotubes for paint degradation

ZnS [72], TiO_2 [73], and Ag [74], decorated HNTs can be utilized as adsorbents with the capacity to remove cationic paints. A novel HNTs–CdS nanocatalyst was once synthesized via utilizing the hydrothermal method with direct growth of CdS nanoparticles on the surface of HNTs [75], the photocatalysis did not exhibit better with increasing adsorption because of the larger adsorption led to a lower transfer mass on the surface of the HNTs–CdS. From the above, adsorption can definitely have an effect on the photocatalysis reaction in all techniques of photodegradation, which was the main control procedure for removing the pollutants [76].

3. EXPERIMENTAL

3.1 Chemicals

3.1.1 Dehydrated castor oil fatty acid (DCOFA)

DCOFA was obtained from Sorel Chemical Industry Products with a liquid at room temperature. It had a water-white to pale yellow color. Its specifications are; refractive index 1.473-1.477 (25°C), specific gravity 0.903-0.905 (25°C), color 2 max (Gardner), acid value 195-205 and iodine value min. 130. DCOFA based alkyd resins and polyamides make up superior constituent in several paints and printing inks formulations and it is also used in the manufacture of high solid alkyds, acrylic and epoxy ester resins. DCOFA was used for synthesis of epoxy ester resin.

3.1.2 Zirconium octoate (12%)

Zirconium octoate was used as driers which was supplied from Ege Kimya. It contains 12% zirconium metal.

3.1.3 Solid epoxy resin

Solid epoxy resin, which was based on bisphenol A and it was unmodified. Its specifications are; epoxy value 1.12 - 1.20 eq/Kg, weight per epoxide 835 - 895 g/Eq, viscosity 550 - 700 mPa.s (25°C) and color 1 max (Gardner). It shows high and uniform rate of esterification, when mixed with diverse fatty acids, due to this property it was used for synthesis of epoxy ester resin. Epoxy resin was obtained from Jubail Chemical Industries Company.

3.1.4 Xylene

Xylene was obtained from Tekkim Kimya San. Tic. Ltd. Şti. and used as a solvent. It is including 3 isomers (o-Xylene, p-Xylene and m-Xylene). Xylene boiling point is 138.5°C and molar mass 106.16 respectively.

3.1.5 Titanium dioxide

Rutile titanium dioxide was selected and it was supplied from The Chemours Company. It was manufactured by the chloride process and was supplied as a fine, dry powder by the company.

3.1.6 Blanc fixe

Blanc fixe was obtained from Solvay which was used as an extender for the production of paints. That blanc fixe has good dispersion properties and its average particle size is 0.8 μm.

3.1.7 Talc

Talc was preferred as an extender for paint production. It was provided from Ertekin Kimya. Talc can be used to improve corrosion resistance and paint adhesion.

3.1.8 Lithopone

Lithopone was obtained from Hebei Yuhuan Chemical Co. Ltd. that was used as a white pigment powder.

3.1.9 Black iron oxide

Black iron oxide was selected as a black pigment and it has excellent UV stability which was supplied from Alpha Chemicals.

3.1.10 Calcium octoate (5%)

Calcium octoate was used as a driers that was supplied from Ege Kimya. It contains 5% calcium and it is also useful as pigment wetting, dispersing agents and helps to improve hardness.

3.1.11 Cobalt octoate (6%)

Cobalt octoate was used, due to it is most efficient surface drier. Its metal content is nearly 6%, it was obtained from Ege Kimya.

3.1.12 Melamine resin

Melamine resin was added to oven curing paint due to its properties like durable, hard and reactive, exhibits chemical resistance. Resin was supplied from Nuplex

Industries Ltd.

3.1.13 Solvesso 100

Solvesso 100 is an aromatic solvent that was used for paint production as a solvent. This aromatic solvent offers high solvency and controlled evaporation characteristics. Its density was 0.879 g/ml, distillation range was between 164-180^{o}C and aromatic content was %99. Solvesso 100 was provided from Soditaş A.Ş.

3.1.14 Rheological additive

Rheological additive has some important properties such as increasing viscosity, providing thixotropy and preventing pigment settling during storage. For these reasons this additive was used for paint production which was supplied from Elementis plc.

3.1.15 Moisture scavanger

Moisture scavenger was obtained from W. R. Grace & Co.-Conn. In metallic and zinc-rich paints, water reacts with the very active metallic pigments such as zinc or aluminum, forming hydrogen. This effect can be avoided by the use of moisture scavenger so it was selected for zinc rich air drying exhaust paint.

3.1.16 Methyl ethyl ketoxime (MEKO)

Methyl ethyl ketoxime, was used as an anti-skinning agent in paints that was supplied from Honeywell International, Inc. MEKO functions via binding the drying agents, metallic salts that catalyze the oxidative crosslinking of drying oils.

3.1.17 Zinc powder

Zinc powder was provided from TNC Corporation. It was used as a protective pigment in air drying exhaust paint.

3.1.18 Halloysite

Halloysite was supplied from Eczacıbaşı Esan, its particle size less than 100 mm. Halloysite was added to paints as a natural nano additive material. Its chemical formula was given as $Al_4Si_4O_{10}(OH)_8.4H_2O$.

3.2 Equipments

3.2.1 Heater

Electrothermal EM Series Electromantles Model can maximum heat transfer to the sample which is achieved by having good insulation. Heater was used for epoxy ester production.

3.2.2 Vacuum oven

Bruker FD 56 model vacuum oven can be heated to a maximum temperature of 300^{o}C. Oven was used for determination of amount of solid and curing.

3.2.3 Digital mechanical stirrer

IKA RW 20 model stirrer has two speed ranges for universal use from 60 - 2.000 rpm. Stirrer was used for epoxy ester synthesis.

3.2.4 Color measurement device

The Tintometer Limited Lovibond device was used and the scale ranges from a pale yellow to a red in shade which is described in terms of the values 1-18. Due to this device epoxy ester Gardner color was seen.

3.2.5 Dispermat dissolver

VMA-Getzmann Dispermat dissolver CN40 (Figure 3.1) was a main equipment to prepare paints. Basket mill was added to dispermat for reduce paint μ because industrial paint must be maximum 15 - 20 μ.

Figure 3.1 : VMA-Getzmann dispermat dissolver CN40.

3.2.6 Grindometer

ECSLAB Grindometer (Figure 3.2) was used to determine how finely ground the particles of pigment (or other solid) dispersed in a sample of paint (or other liquid).

Figure 3.2 : ECSLAB grindometer.

3.2.7 Viscometer

Brookfield engineering. KU-2 model viscometer offers digital calculating for paint products as a Krebs Unit. It has expanded measurement range (40 to 141 KU).

3.2.8 Drying time recorder

Sheen Instruments SHBK3 model drying time recorders was used to determination of drying time for paints and epoxy ester. It is holding six hemispherical ended needles travels the length of the six 305 x 25 mm test strips in 6, 12 or 24 hours.

3.2.9 Gloss meter

Paints and epoxy ester gloss was measured using by BYK micro-gloss model (Figure 3.3). The ratio for the gloss standard, was recorded as gloss units (GU) and three measurement angles (20°, 60°, and 85°) values were recorded.

Figure 3.3 : BYK micro-gloss model gloss meter.

3.2.10 Pendulum hardness tester

BYK pendulum hardness tester (Figure 3.4) is a hardness measuring instrument in accordance with the König which was used for paints and epoxy ester.

Figure 3.4 : Byk pendulum hardness tester.

3.2.11 Adhesion tester

Sheen Instruments cross hatch cutter model (Figure 3.5) adhesion tester is for detecting the resistance of paint and epoxy ester to separation from substrates when a right angled lattice pattern is cut into the paint.

Figure 3.5 : Sheen cross hatch cutter.

3.2.12 Impact tester

BYK-Gardner ISO impact tester (Figure 3.6) was used for testing impact resistance of paints and epoxy ester on metal substrates. It works according to the principle of weight falling on the paint surface.

Figure 3.6 : BYK-Gardner ISO impact tester.

3.2.13 Flexibility tester

The Paul N. Gardner Company, Inc. (GARDCO) conical mandrel tester (Figure 3.7) was used for easy and short testing of the flexibility of a paint through bending a lined panel over a rod of regarded diameter after which examining the paint for cracking, flaking, or other damage.

Figure 3.7 : Gardco conical mandrel tester.

3.2.14 Spectrophotometer

Coverage ability of paint was measured by Shimadzu UV-2600 model spectrophotometer.

3.2.15 Corrosion tester

Erichsen salt spray (fog) tester (Figure 3.8) was used to determine corrosion deformation of paints under accelerated conditions. This cyclic corrosion tests provides much better information on the relative degree of corrosion than e. g. pure salt spray fog tests.

Figure 3.8 : Erichsen salt spray (fog) tester.

3.2.16 Thermogravimetric analyzer

Perkin Elmer TGA 4000 model has 1000 °C maximum temperature and it was used to determine thermal characterization of all paints.

3.2.17 Pycnometer

Erichsen pycnometer was used determine the density of paints. Apparatus had 100 ml capacity and was made from steel.

3.3 Experimental Procedure

3.3.1 Synthesis of epoxy ester resin

Epoxy ester resin was selected as a binder of paints. For the preparation of epoxy ester; firstly, 22-23% wt DCOFA and 0.2% wt zirconium octoate (12%) were weighed and were put into 5 liter reaction balloon. Then, heater and digital mechanical stirrer was opened. Heating was maintained until 90-100 °C, when

temperature reached this level, 38-39% wt solid epoxy resin was added to balloon and temperature was increased to 240°C. Reflux solvent, which was 2% wt xylene, was added on 160°C gradually.

Reflux and first water out were seen aproximately at 230°C. When temperature reached 240°C, taking sample for acid, viscosity and solid values control was started. Acid value was controlled according to ISO 2114 (Determination of partial acid value and total acid value) as a mg KOH/g resin unit. Solid was tested according to ISO 3251(Determination of non-volatile-matter content) and viscosity was tested according to ASTM D1545 (Standard test method for viscosity of transparent liquids by bubble time method) as a Gardner-Holdt second. Taking sample was repeated every half hour up to 3 mg KOH/ g resin acid. According to resin specification solid 59-61% and viscosity 18-33 second had to have. If these specification values are not reached, a formulation change is made. When resin reached these values, the system was cooled up to 130°C. At this temperature, main solvent, that was 38% wt xylene was added gradually and mixed about 30 minutes. Finally, resin was poured with the filter.

3.3.2 Testing of epoxy ester resin

Drying time, gloss, adhesion, flexibility, hardness and impact tests were applied to epoxy ester. Before these test few amount of epoxy ester was converted to varnish by adding driers combination (Zr Oct. (12%), Ca Oct. (5%) and Co Oct. (6%)) for performance testing.

For the determining of drying time of epoxy ester (TS 4317 - Drying, curing or film formation of organic coatings at room temperature), varnish was applied to glass surface with 60 µ and it was checked manually. In order to assess gloss of epoxy ester (ASTM D523 – 14 - Standard test method for specular gloss), varnish was applied to glass surface with 120 µ which was tested by gloss meter. For considering adhesion performance of epoxy ester (ISO 2409 - Cross-cut test), varnish was applied to metal surface with 120 µ then it was tested by cross hatch cutter. In order to determine flexibility of epoxy ester (ISO 6860 - Bend test (conical mandrel)), varnish was applied to metal surface with 120 µ and it was checked by cylindrical mandrel tester. For considering hardness of epoxy ester (DIN EN ISO 1522 - Pendulum damping test), varnish was applied to glass surface with 120 µ which was

tested by pendulum hardness tester. In order to determine impact performance of epoxy ester (ASTM D2794 - Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation) , varnish was applied to metal surface with 120 μ then it was tested by impact tester.

Lastly, in order to measure color of epoxy ester resin (ISO 4630-2 - Estimation of color by the Gardner color scale -- Part 2: Spectrophotometric method) which was diluted by xylene up to 50% solid content, after it was checked with color measurement device.

3.3.3 Preparation of air drying exhaust paints with halloysite additive

Epoxy ester resin, which had been produced earlier, was used as a binder for this paint. The production process consisted of the following stages. Firstly, 13% wt epoxy ester was stirred for 10 minutes at 750 rpm by dispermat dissolver.

Then 0.1% wt calcium octoate and 0.8% wt rheological additive were added and mixed for 10 minutes at 1000 rpm. 69-70% wt zinc powder was given slowly at this stage. Amount of xylene, that will be given, was divided two parts. First part xylene was added at this stage and stirred under 1500 rpm nearly 15 minutes.

At the next stage paint was grinded by basket mill for 20 minutes at 4000 rpm and grinding was controlled by grindometer. Afterwards, 0.5% wt moisture scavenger, 0.8% wt solvesso 100 and 0.1% wt cobalt octoate were put into the paint under 750 rpm for 10 minutes. In the final stage, 0.1% wt methyl ethyl ketoxime was added under 40°C and was mixed at low rpm in a short time.

Thus air drying paint was completed and approximately 2 liter total paint was distributed in five gallon. First gallon does not contain any halloysite to check halloysite effect on this type of paint. 1% wt halloysite was calculated according to the amount of paint in second gallon and halloysite was added into gallon at 500 rpm in a 5 minutes. 2% wt halloysite was put into third gallon and mixed for 5 minutes at 500 rpm. 5% wt halloysite was added slowly into fourth gallon and stirred at 500-600 rpm in a 5-7 minutes. Finally, for the fifth gallon 10% wt halloysite was loaded much more slowly, mixed at 600 rpm in a 5-7 minutes. Five gallons were numbered according to the table (Table 3.1) below.

Table 3.1 : Air drying exhaust paint numbers.

Air Drying Exhaust Paint	**Numbers**
Air drying exhaust paint	A1
Paint + 1% Halloysite	A2
Paint + 2% Halloysite	A3
Paint + 5% Halloysite	A4
Paint + 10% Halloysite	A5

3.3.4 Preparation of oven curing metal paint with halloysite additive

Epoxy ester resin, again was used as a binder for this paint. For the preparation of oven curing metal paint; primarily, 27% wt epoxy ester was mixed on its own for 10 minutes at 750 rpm by dispermat dissolver. Then 0.3% wt calcium octoate were added and mixed for 10 minutes at 1000 rpm. 12% wt titanium dioxide was given at this steps and rpm was increased to 1500. After 15 minutes from the titan has been added, 9% wt blanc fixe, 0.2% wt black iron oxide and 4% wt lithopone were given respectively. Then 6.5% wt talc was given and rpm was maintained at 1500. Next stage was basket mill stage, paint was grinded by basket mill for 20 minutes at 4000 rpm and grinding was controlled by grindometer. When paint grinding was completed, remaining 28% wt epoxy ester resin was added to the gallon. In this stage, other ingredients which were 5% wt melamine resin and 8% xylene, were added to paint and mixed under 750 rpm for 15 minutes. Thus, the paint was completed.

Again nearly 2 liter total paint was divided in five gallon. First gallon does not contain any halloysite to check halloysite effect on this type of paint. 1% wt halloysite was calculated according to the amount of paint in second gallon and halloysite was added into gallon at 500 rpm in a 5 minutes. 2% wt halloysite was put into third gallon and mixed for 5 minutes at 500 rpm. 5% wt halloysite was added slowly into fourth gallon and stirred at 500-600 rpm in a 5-7 minutes. Finally, for the fifth gallon 10% wt halloysite was loaded much more slowly, mixed at 600 rpm in a 5-7 minutes. Five gallons were numbered according to the table (Table 3.2) below.

Table 3.2 : Oven curing metal paint numbers.

Oven Curing Metal Paint	**Numbers**
Oven curing metal paint	O1
Paint + 1% Halloysite	O2
Paint + 2% Halloysite	O3
Paint + 5% Halloysite	O4
Paint + 10% Halloysite	O5

3.3.5 Testing of paints

Tests were applied to 10 prepared paints, that were numbered and described earlier. First of all, air drying exhaust paints (A1, A2, A3, A4, A5) and oven curing metal paints (O1, O2, O3, O4, O5) supposed to have nearly same viscosity among themselves so air drying paints and oven curing paints were diluted with xylene or maintained to have same viscosity each other. This was tested by viscometer as a Krebs Unit, according to ASTM D562-10 (Standard test method for consistency of paints measuring Krebs Unit (KU) viscosity using a stormer-type viscometer).

For determining the effects of halloysite on the densities of paints, ASTM D1475-13 (Standard test method for density of liquid coatings, inks, and related products) was taken as a reference. Pycnometer was weighed when it was empty and was filled with paint, then was capped, left the overflow. Immediately got rid of excess overflowed in depressions by wiping dry with absorbent fabric. Lastly filled pycnometer was weighed again and numbers were recorded.

For evaluating the effects of halloysite on the solids of paints, paints were tested according to ASTM D2369-10 (Standard test method for volatile content of coatings). Empty aluminum foil dishes were weighed and recorded the weight to the nearest 0.1 mg with analytical balance. Then nearly 2 gram paint was weighed, this procedure was repeated 2 times for each paints. Heated the aluminum foil dishes containing the specimens in the vacuum oven for 60 min. at 110°C. Removed each dish from the oven, placed immediately in a desiccator, cooled to ambient temperature, weighed with the 0.1 mg precisely and recorded this weight for each specimen.

In order to examine the effects of halloysite on the coverage values of paints, that were controlled with ISO 2814 (Comparison of contrast ratio (hiding power) of paints of the same type and color) . Paint was utilized to checkerboard card, paint film was taken 50 µ by film applicator. Only oven curing paint film cards were kept in the oven for 30 minutes at 150°C. After one day coverage values were detected for all paints by spectrophotometer device.

For determining the effects of halloysite on the gloss values of paints, ASTM D523-14 (Standard test method for specular gloss) was taken as a reference. Substrate surfaces were glass. 200 µ paint film was utilized to these surfaces due to film applicator. Oven curing paint films were cured in the oven for 30 minutes at 150°C. The next day, was taken at least three readings. Beam axis angles (20°, 60°, or 85°) were recorded for all paints from the glossmeter.

For evaluating the effects of halloysite on hardness values of paints, DIN EN ISO 1522 (Pendulum damping test) was selected. Paint films were applied to glass surfaces 100 µ by film applicator. Again, oven curing paint films were kept in the oven for 30 minutes at 150°C for curing. After one day, results were tested by pendulum hardness tester for all paints.

Drying time is not available for oven curing paint, because it cannot dry with oxidation. For determining the effects of halloysite on the drying times of air drying exhaust paints, that kind of paints were applied to glass test strips as 100 µ by film applicator. After the films were taken, test strips were placed on the drying time recorder and device was set to 24 hours. TS 4317 (Drying, curing or film formation of organic coatings at room temperature) was taken as a reference. After 24 hours, paints were removed from the machine and the drying times were noted.

In order to examine the effects of halloysite on the impact resistances of paints, ASTM D2794 (Standard test method for resistance of organic coatings to the effects of rapid deformation (Impact)) was used. According to this standart, firstly metal substrate surfaces was sanded then paint films were utilized to these surface by film applicator, which was 90 µ. Oven curing paint films were cured in the oven for 30 minutes at 150°C. Seven days later, all paint films were subjected to impact resistance test. In this test, semi-spherical shape which had 0.2 kg, was dropped onto horizontal painted panel. Until deterioration in the paint film (cracking, blistering,

flaking) was occurred, the height of the spherical to be increased by slightly more weight every time. This test was applied for the front (direct) and back (indirect) surface of the paint. Paint film impact resistance was taken as the maximum height of the applied load without any distortion.

For evaluating the effects of halloysite on the adhesion values of paints, paints were tested according to TS EN ISO 2409 (Cross-cut test) on galvanized, copper, sheet iron, and aluminum surfaces. Primarily sheet iron surfaces were sanded but other surfaces were not sanded only cleared by acetone. All paints were applied to these four different surfaces. Paint films were taken 120 µ by film applicator. All oven curing paint surfaces were kept in the oven for 30 minutes at 150°C. After 4 days, all paint films were tested. Cutting tool was holded to the test panel surfaces. With uniform pressure on the cutting tool and made number of parallel cuts on the paint films at a uniform cutting rate. This operation was repeated, made further parallel cuts of equal number. Brushed the test panel surfaces lightly with the soft brush. Then adhesion tapes were sticked to surfaces completely and were pulled quickly. After tape was removed, the adhesion performances of the paints were noted.

For determining the effects of halloysite on flexibilities of paints, ISO 6860 (Bend test (conical mandrel)) was used as a reference. Paint films were utilized to metal surfaces 150 µ by film applicator. Oven curing paint films were kept in the oven for 30 minutes at 150°C. At the end of the third day, all paints were controlled by conical mandrel tester. In conical bending test; conical panels were twisted 180 degrees around a mandrel in 15 seconds. Finally paints were assessed as pass or fail.

For evaluating the effects of halloysite on the corrosion resistances of paints, this test were checked according to ASTM B117-16 (Standard practice for operating salt spray (fog) apparatus). Primarily all paints were diluted by xylene to application viscosities, because paint pistol was used. Oven curing paint films were again left for 30 minutes at 150°C. After one week, painted surfaces were taped from their edges. One of the two surfaces were drawn with a box cutter for one paint. The salt solution prepared by dissolving 5 parts by mass of sodium chloride in 95 parts of water. The exposure zone of the salt spray chamber set at 35°C. Then all paints, were placed in a salt spray chamber. Painted surfaces, that were checked every week, approximately 500 hours were kept in the device. After 500 hours, paints were removed from chamber and corrosion performance were evaluated.

Finally, in order to determine the effects of halloysite on the thermal resistances of paints, TGA was utilized to all paints. Thermogravimetric analyzer includes pan that was weighed firstly and paint was put into this pan. The thermal behavior of the paint was viewed from the monitor up to 900 degrees at a heating rate 20 °C/min.

4. RESULTS AND DISCUSSION

4.1 Epoxy Ester Synthesis and Test Results

During epoxy ester synthesis, acid, solid and viscosity target values which were one of the monitored parameters has been reached. As shown in the table, acid, solid, viscosity, color and drying time results were within the specification values. According to Table 4.1, it was determined that, epoxy ester does not have a high hardness and showed high gloss and gloss retention. Furthermore, this epoxy ester resin was showed good flexibility and good adhesion with high impact resistance.

Table 4.1 : Epoxy ester synthesis and test results.

Test	Reference Method	Target	Result
Solid (%)	ISO 3251	59-61%	59.5
Acid value (mg KOH/g resin)	ISO 2114	3 max.	1.6
Viscosity* (sec GBT/23 °C)	ASTM D1545	18-33	22
Viscosity** (GH)	ASTM D1545	X-Z (60% Xylene)	X-Y
Color (Gardner -50%)	ISO 4630-2	6 max.	2.9
Drying time (min.)	TS 4317	60 max.	45
Hardness (König)	ISO 1522		17
Gloss (20°- 60°- 85°)	ASTM D523 – 14		135-133-105
Flexibility	ISO 6860		Passed
Adhesion (Gt)	ISO 2409		Gt-1 (very good)
Impact Resistance	ASTM D2794		Direct up to 30 cm Indirect up to 100 cm

* Gardner-Holdt second

****** Gardner-Holdt unit

4.2 Paint results

4.2.1 Viscosity results

As previously stated, paints, that belong to the same curing group (air drying or oven curing), their viscosities was adjusted by xylene to be close to each other. Final

viscosity values were showed in the following table (Table 4.2). O4 and O5 were showed higher viscosity so they were diluted with few xylene to have a similar viscosity values. It is observed that the halloysite increases the viscosity of the paint.

Table 4.2 : Results the viscosities of the paints.

Air Drying Exhaust Paint	Viscosity (KU)	Oven Curing Metal Paint	Viscosity (KU)
A1	75	O1	104.8
A2	75	O2	105.5
A3	74.2	O3	106.2
A4	75.3	O4	106.6
A5	75.4	O5	106.6

4.2.2 Density results

The densities of the paints were shown in the following table (Table 4.3). Air drying paint has higher density than the oven curing paints, because air drying paint contains high amounts of zinc. Air drying paint densities was decreased, when halloysite was added. Due to the density of halloysite (2 - 2.65 g/cm^3) is quite less as compared to zinc (7.14 g/cm^3), halloysite was reduced the density of air-drying paints. Oven curing paints have significantly lower density than air drying paints, because these paints do not contain zinc. Therefore, with the increased amount of halloysite it was observed that the density increased.

Table 4.3 : Results the densities of the paints.

Air Drying Exhaust Paint	Density (g/mL)	Oven Curing Metal Paint	Density (g/mL)
A1	2.43	O1	1.26
A2	2.39	O2	1.27
A3	2.37	O3	1.27
A4	2.36	O4	1.28
A5	2.29	O5	1.30

4.2.3 Solid results

According to following solid results table (Table 4.4), it is observed that halloysite has an impact on the amount of solid. It was shown that amount of solid was reduced by the addition of halloysite for the air drying exhaust paint. On the other hand, there is no prominent tendency in oven curing metal paint. Because when halloysite was added, solid results were independent of each other, this situation can be seen from the table (Table 4.4).

Table 4.4 : Results the solids of the paints.

Air Drying Exhaust Paint	Solid (%)	Oven Curing Metal Paint	Solid (%)
A1	80.2	O1	66.8
A2	79.8	O2	67.3
A3	79.8	O3	66.0
A4	79.6	O4	66.3
A5	78.9	O5	67.3

4.2.4 Coverage results

Coverage values were investigated with the addition of halloysite. Both paints (air drying & oven curing) are shown very high coverage without halloysite. These values can be seen from the Table 4.5, which were more than 99%. That means both paints have excellent coverage. It is to be mentioned here halloysite did not create a negative impact on the coverage.

Table 4.5 : Results the coverage values of the paints.

Air Drying Exhaust Paint	Coverage (%)	Oven Curing Metal Paint	Coverage (%)
A1	99.99	O1	99.89
A2	99.99	O2	99.41
A3	99.98	O3	99.77
A4	99.99	O4	99.54
A5	99.99	O5	99.48

4.2.5 Drying time and curing results

Drying time were checked for only air drying paints. When considering the effect of halloysite on the paint drying time, one of the most important things halloysite should not delay drying time. According to Table 4.6, halloysite was not accelerated drying time but it was retained drying time.

Table 4.6 : Results the drying times of the paints.

Air Drying Exhaust Paint	Touch Dry (min.)	Full Dry (min.)
A1	10	650
A2	12	660
A3	10	660
A4	10	650
A5	9	660

Oven curing paints have completed their curing within 30 minutes at 150°C. The amount of halloysite was increased that was added to oven curing paints it was observed that cracks in the paint film reduced to a minimum level. According to this, it can be said that paint film was protected by halloysite against the high temperature.

4.2.6 Gloss results

According to the gloss test with a glossmeter, air drying paints were found to be quite matt paint. Along with the increase of the amount of halloysite it was seen that from the table 4.7 the opacity of the air drying paint has not been almost effected by haloysite, only A5 was showed an increase of 1 gloss at 85°. Accordance with to the results of gloss oven curing paints (Table 4.7) were entirely different from the air drying paint. Oven curing paints were found glossy. If we determine to the effects of the halloysite in the oven curing paint, quite an increase was observed in the 20°. This increase was monitored at 60° and 85° but a little less. The increased in the amount of halloysite for this paint increased the gloss of the paint. Halloysite reduced the roughness on the surface, increased the reflection thus gloss of paint increased.

Table 4.7 : Results the gloss values of the paints.

Air Drying Exhaust Paint	Gloss (20°- 60°- 85°)	Oven Curing Metal Paint	Gloss (20°- 60°- 85°)
A1	0.2 – 0.7 – 1.1	O1	36.4 – 80.8 – 90.9
A2	0.1 – 0.7 – 1.1	O2	47.5 – 83.6 – 92.7
A3	0.1 – 0.7 – 1.0	O3	45.4 – 85.2 – 92.9
A4	0.1 – 0.6 – 1.2	O4	45.6 – 85.2 – 91.7
A5	0.2 – 0.6 – 2.0	O5	42.3 – 81.9 – 91.4

4.2.7 Hardness results

When analyzing the results of the hardness of paints (Table 4.8), it has been shown that the hardness of paints affected by halloysite. Air drying paint without halloysite has high hardness because it contains pretty much zinc, therefore, the amount of halloysite added increases, a reduction in hardness were seen. Oven curing paint without halloysite has normal hardness value, as expected, an increase in the concentration of halloysite increased the hardness of paints. Due to this feature, the hardness increased for oven curing paint with addition of halloysite.

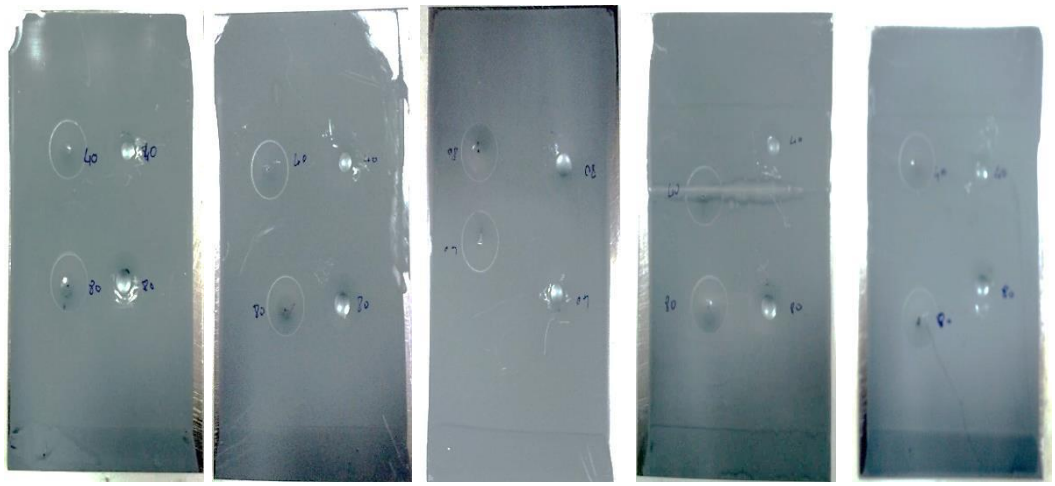
Table 4.8 : Results the hardness values of the paints.

Air Drying Exhaust Paint	Hardness (König)	Oven Curing Metal Paint	Hardness (König)
A1	70	O1	40
A2	59	O2	40
A3	30	O3	42
A4	30	O4	49
A5	37	O5	50

4.2.8 Impact resistance results

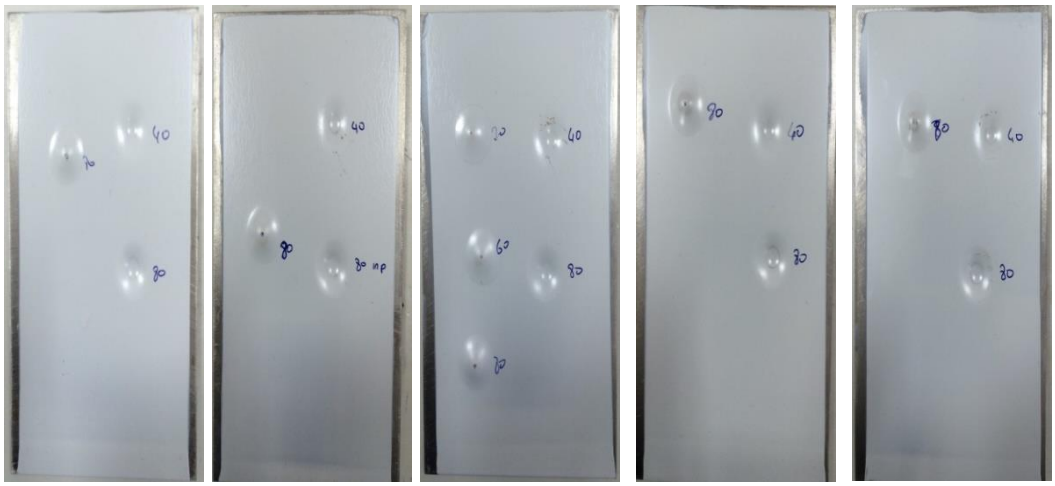
Before begin to test the impact resistance of paints, it was estimated that paint with the increased amount of halloysite, will increase the impact resistance. Because halloysite can incorporate in a epoxy ester resin to increase the mechanical properties. Also epoxy resin can be tough with a halloysite. Each different curing

paints have shown excellent results in the impact resistance test even without the halloysite added. For these paints, falling weight was left from the highest point but paint films were not showed any cracking or deforming. Added halloysite in the paints have shown resistance to this highest point in the same way, has not seen cracked or deformed on paint films. Therefore, halloysite could not shown any effects on the impact resistance of these different curing paints. The following pictures (Figure 4.1, 4.2) and table (Table 4.9) illustrates the results of impact tests.



A1 **A2** **A3** **A4** **A5**

Figure 4.1 : Air drying exhaust paints impact resistance results.



O1 **O2** **O3** **O4** **O5**

Figure 4.2 : Oven curing metal paints impact resistance results.

Table 4.9 : Results the impact resistances of the paints.

Air Drying Exhaust Paint	Impact Res. (cm)	Oven Curing Metal Paint	Impact Res. (cm)
A1	Direct & Indirect >80cm	O1	Direct & Indirect >80cm
A2	Direct & Indirect >80cm	O2	Direct & Indirect >80cm
A3	Direct & Indirect >80cm	O3	Direct & Indirect >80cm
A4	Direct & Indirect >80cm	O4	Direct & Indirect >80cm
A5	Direct & Indirect >80cm	O5	Direct & Indirect >80cm

4.2.9 Flexibility results

Flexibility were investigated with the addition of halloysite. Before tests are made, the halloysite was unknown how it will affect the flexibility of the paint. According to the results two different curing paints that does not include halloysite, have shown great flexibility even though these paints does not contain any plasticizer. The adhesion property and epoxy ester content of the paints have a direct impact on the flexibility of paints. Good adhesion and oil contents from epoxy ester resin tends to gives good flexibility. The reasons for this, air drying paint showed excellent flexibility because it can easily adhere to substrate surface by interacting with zinc molecules. Oven drying paint has high epoxy ester content this is one of the reason why this paint showed high flexibility other reason is, this paint has great adhesion property because their curing was completed with a oven. When examined the effect of halloysite on two different curing paints, it was seen that halloysite did not have any positive or negative effects. According to following pictures (Figure 4.3, 4.4) and table (Table 4.10) all paints has passed flexibility test.

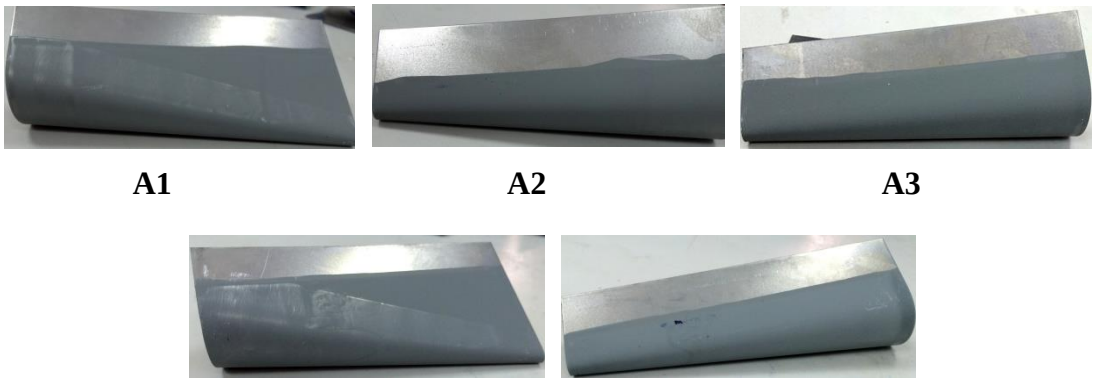


Figure 4.3 : Air drying exhaust paints flexibility test results.

Figure 4.4 : Oven curing metal paints flexibility test results.

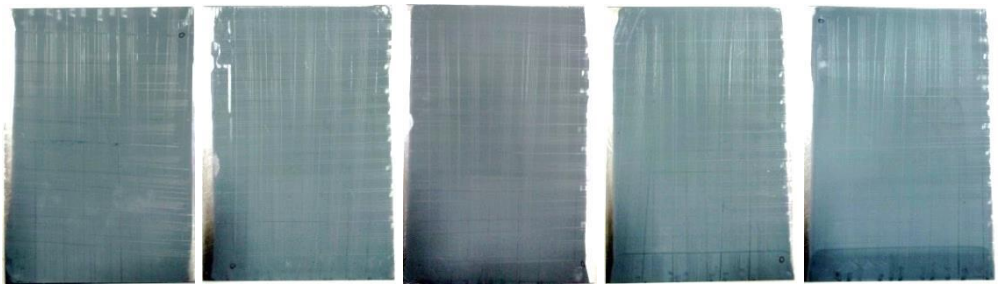
Table 4.10 : Results the flexibilities of the paints.

Air Drying Exhaust Paint	Flexibility	Oven Curing Metal Paint	Flexibility
A1	Passed	O1	Passed
A2	Passed	O2	Passed
A3	Passed	O3	Passed
A4	Passed	O4	Passed
A5	Passed	O5	Passed

4.2.10 Adhesion results

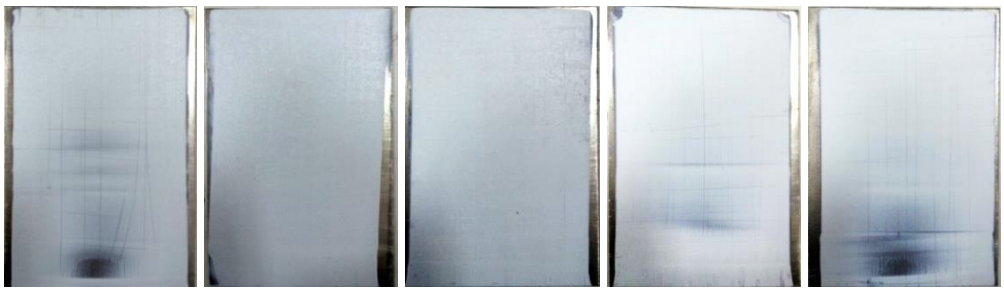
Paint adhesion results were determined after experiments on four different surfaces. According to the pictures (Figure 4.6, 4.8, 4.10, 4.12) as expected, oven curing paints have shown excellent adhesion and air drying paints have shown good adhesion. The reason for this was that binding type of the paints epoxy ester which demonstrates

great adhesion to most surfaces. Oven curing paints contain high epoxy ester content and these paints were stoved therefore they have shown excellent adhesion to all surface. Oven curing paint films were able to evaporate their solvent in the oven so these paints were easily spreaded to surface. Air drying paints always contain few solvents in their paint film because they never exactly drying hence adhesion of these paints were found lower than oven curing paints. It was stated earlier that halloysite has an impact on the hardness of the paint in spite of this, it was seen that halloysite had almost no effect on the adhesion of paints (Figure 4.5 - 4.12). The increase of added halloysite in the oven curing paint, there has been no change for adhesion results. This inference was also available for air drying paint but aluminum surface adhesion results differed from others. Increasing the amount of halloysite was slightly reduced adhesion on the aluminum surface for air drying paints (Figure 4.9). Table 4.11 and 4.12 showed all adhesion results for air drying and oven curing paints.



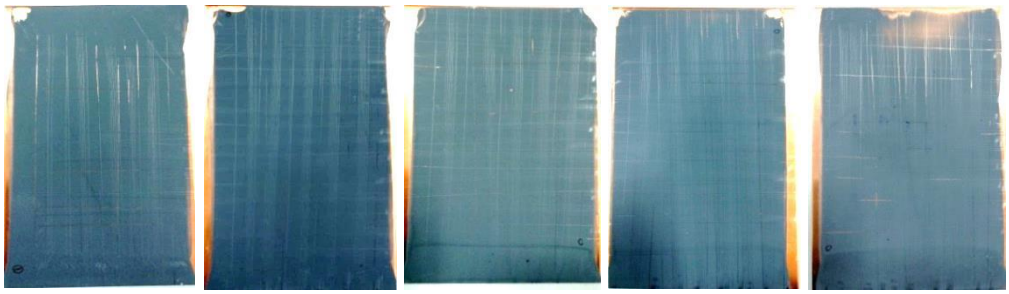
A1 **A2** **A3** **A4** **A5**

Figure 4.5 : Air drying exhaust paints on the sheet iron surfaces adhesion results.



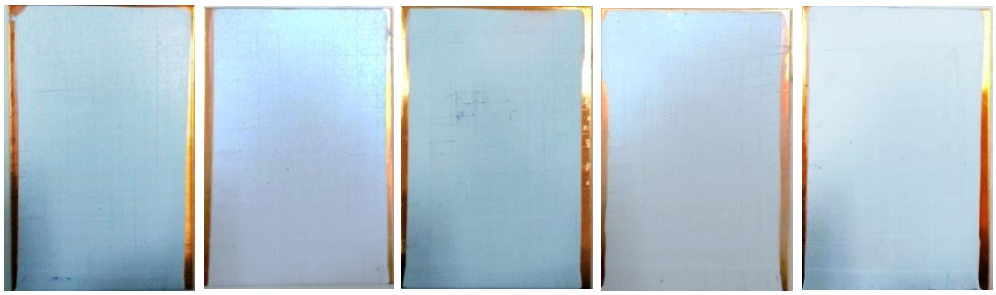
O1 **O2** **O3** **O4** **O5**

Figure 4.6 : Oven curing metal paints on the sheet iron surfaces adhesion results.



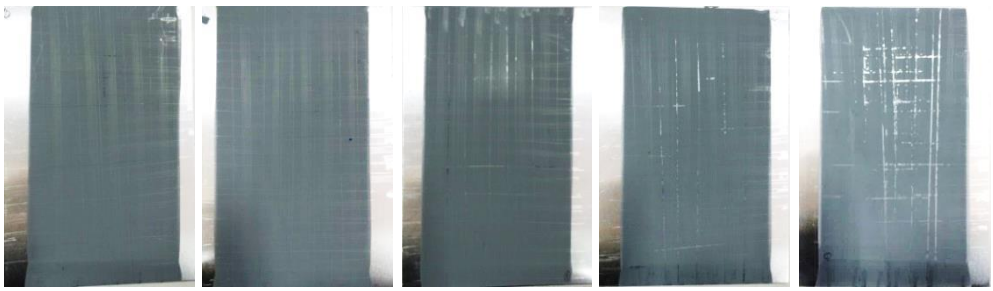
A1 **A2** **A3** **A4** **A5**

Figure 4.7 : Air drying exhaust paints on the copper surfaces adhesion results.



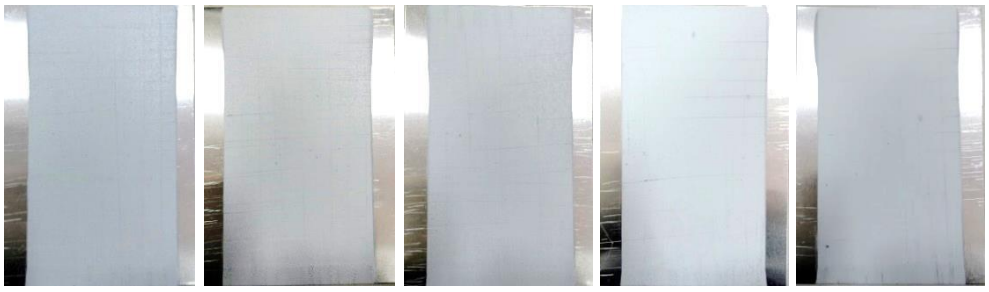
O1 **O2** **O3** **O4** **O5**

Figure 4.8 : Oven curing metal paints on the copper surfaces adhesion results.



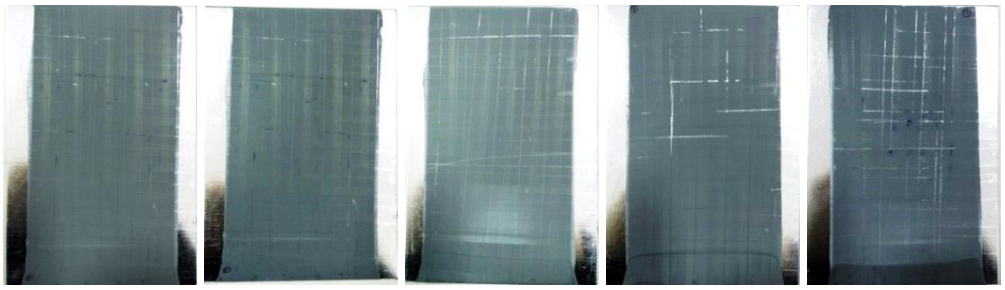
A1 **A2** **A3** **A4** **A5**

Figure 4.9 : Air drying exhaust paints on the aluminium surfaces adhesion results.



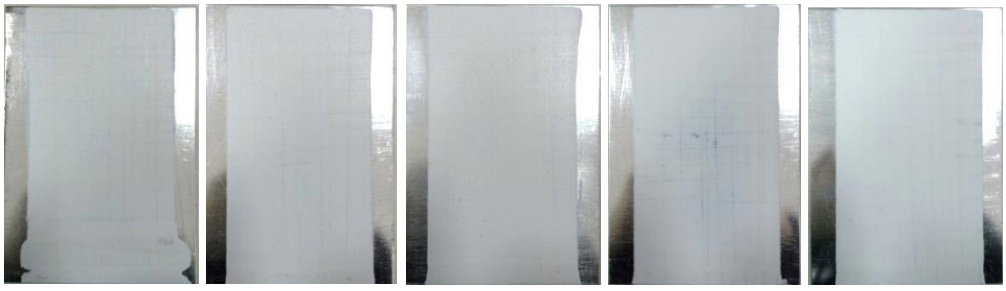
O1 **O2** **O3** **O4** **O5**

Figure 4.10 : Oven curing metal paints on the aluminium surfaces adhesion results.



A1 **A2** **A3** **A4** **A5**

Figure 4.11 : Air drying exhaust paints on the galvanized surfaces adhesion results.



O1 **O2** **O3** **O4** **O5**

Figure 4.12 : Oven curing metal paints on the galvanized surfaces adhesion results.

Table 4.11 : Results the adhesion values of the air drying exhaust paints.

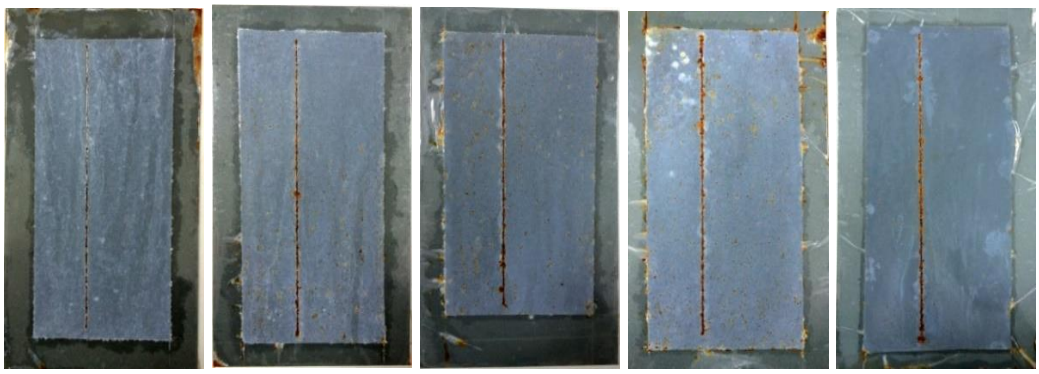
	Iron Sheet	**Copper**	**Aluminium**	**Galvanized**
A1	Gt-0	Gt-0	Gt-0	Gt-1
A2	Gt-0	Gt-0	Gt-0	Gt-1
A3	Gt-0	Gt-0	Gt-1	Gt-1
A4	Gt-0	Gt-0	Gt-1	Gt-1
A5	Gt-0	Gt-0	Gt-2	Gt-1

Table 4.12 : Results the adhesion values of the oven curing metal paints.

	Iron Sheet	**Copper**	**Aluminium**	**Galvanized**
O1	Gt-0	Gt-0	Gt-0	Gt-0
O2	Gt-0	Gt-0	Gt-0	Gt-0
O3	Gt-0	Gt-0	Gt-0	Gt-0
O4	Gt-0	Gt-0	Gt-0	Gt-0
O5	Gt-0	Gt-0	Gt-0	Gt-0

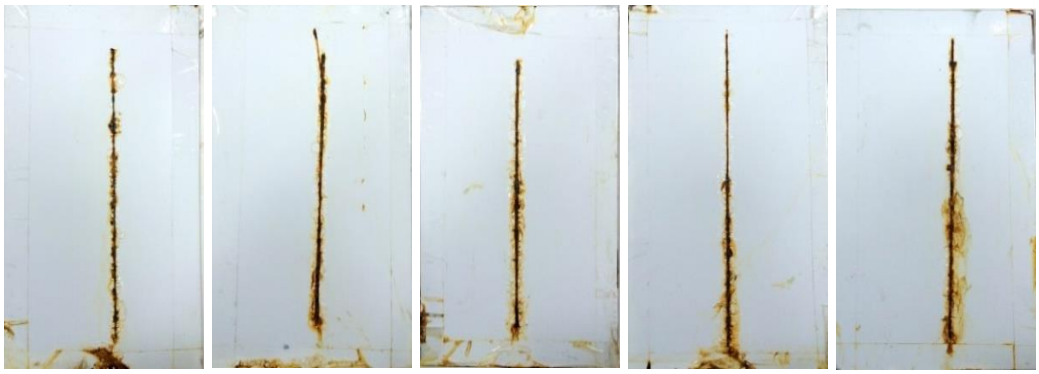
4.2.11 Corrosion (salt spray) results

Epoxy ester resin containing paints have already a good corrosion resistance, therefore air drying and oven curing paints had good corrosion resistance even without other raw materials. Air drying paints and oven curing paints were kept in salt spray chamber 500 hours, in order to see corrosion resistance of paints. 500 hours is quite a long time. According to these following pictures (Figure 4.13, 4.14), air drying paints had higher corrosion resistance than oven curing paints. The reason for this was air drying paint containing quite high amounts of zinc that made cathodic protection due to this zinc paint film protected steel. Thus, the corrosion rate has decreased significantly. Examined corrosion resistance of halloysite added air drying and oven curing paints had not seen an improvement. Accordingly, it was observed that halloysite alone could not contribute to corrosion resistance.



A1 **A2** **A3** **A4** **A5**

Figure 4.13 : Air drying exhaust paints salt spray test results.



O1 **O2** **O3** **O4** **O5**

Figure 4.14 : Oven curing metal paints salt spray test results.

4.2.12 TGA results

The thermal gravimetric analyses of air drying paint and oven curing paint were observed in order to investigate the effects of halloysite. Primarily halloysite free paints were examined, it is observed that air drying paint can withstand higher temperatures than oven curing paint. Inorganic raw materials are more resistant to high temperature rather than organic raw materials. Thus in the formulation of air drying paint contained high amounts of inorganic raw materials so that reason, it had a high resistance against the temperature.

Resistance against temperature for each two types of paint have increased along with the addition of halloysite. Results (Figure 4.15, 4.16) have shown that the thermal decomposition temperature has increased in a positive way with halloysite for two different paint types. For example, if air drying paint examined, after approximately 800 degrees without halloysite paint lost of a large mass but when halloysite was added, temperature resistance has considerably improved. A2 and A3 paints showed better thermal resistance rather than A4 and A5. This may be because the halloysite could not adequately mix. A1 had approximately 62.4% mass loss on the other hand A2, A3, A4 and A5 had respectively 23.6%, 25.74%, 32.8% and 37% mass loss values.

Considering the results of the oven curing paint analysis (Figure 4.16), effect of halloysite on thermal resistance was observed again. Paint that does not contain any halloysite the first breakage point was about at 240°C, this point was close to 300°C as it increases the amount of halloysite added. Second breakage point was nearly 520°C that again increased when halloysite was added. Last remaining masses were respectively 32% (O1), 32.6% (O2), 32.41% (O3), 33% (O4), 35.4% (O5). According to these results, it was observed that the halloysite has a positive impact on thermal resistance of the paint and halloysite provides a better mixing in all proportions rather than air drying exhaust paint.

Finally, when all TGA results are put together, due to flame retardant property, which is theoretically known feature of halloysite, increased thermal resistance of paints. Besides, for oven curing paint, after curing, the properties of the film confirmed it. As mentioned above, halloysite added paints could maintain film structure after came out of the oven.

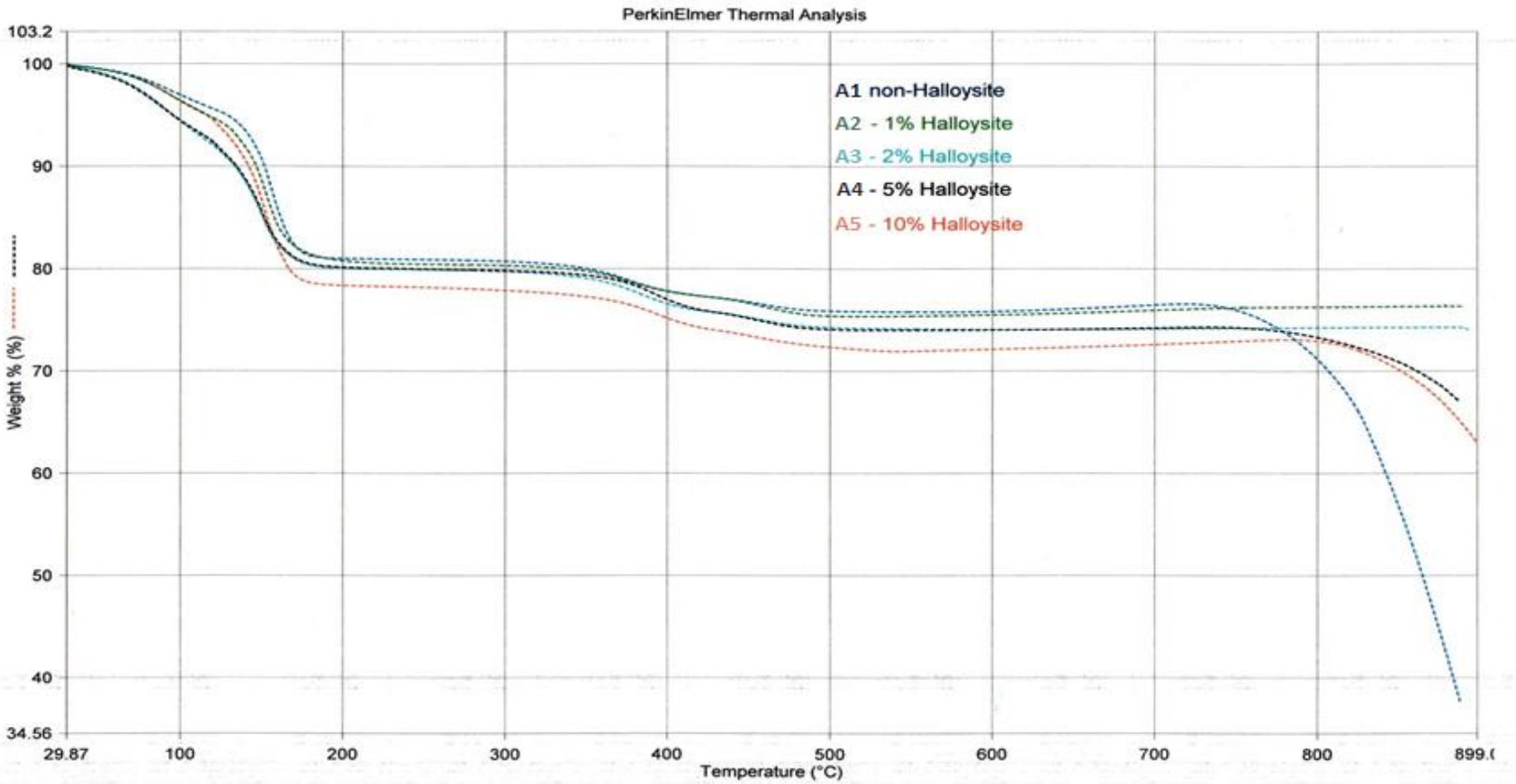


Figure 4.15 : Air drying exhaust paints TGA results.

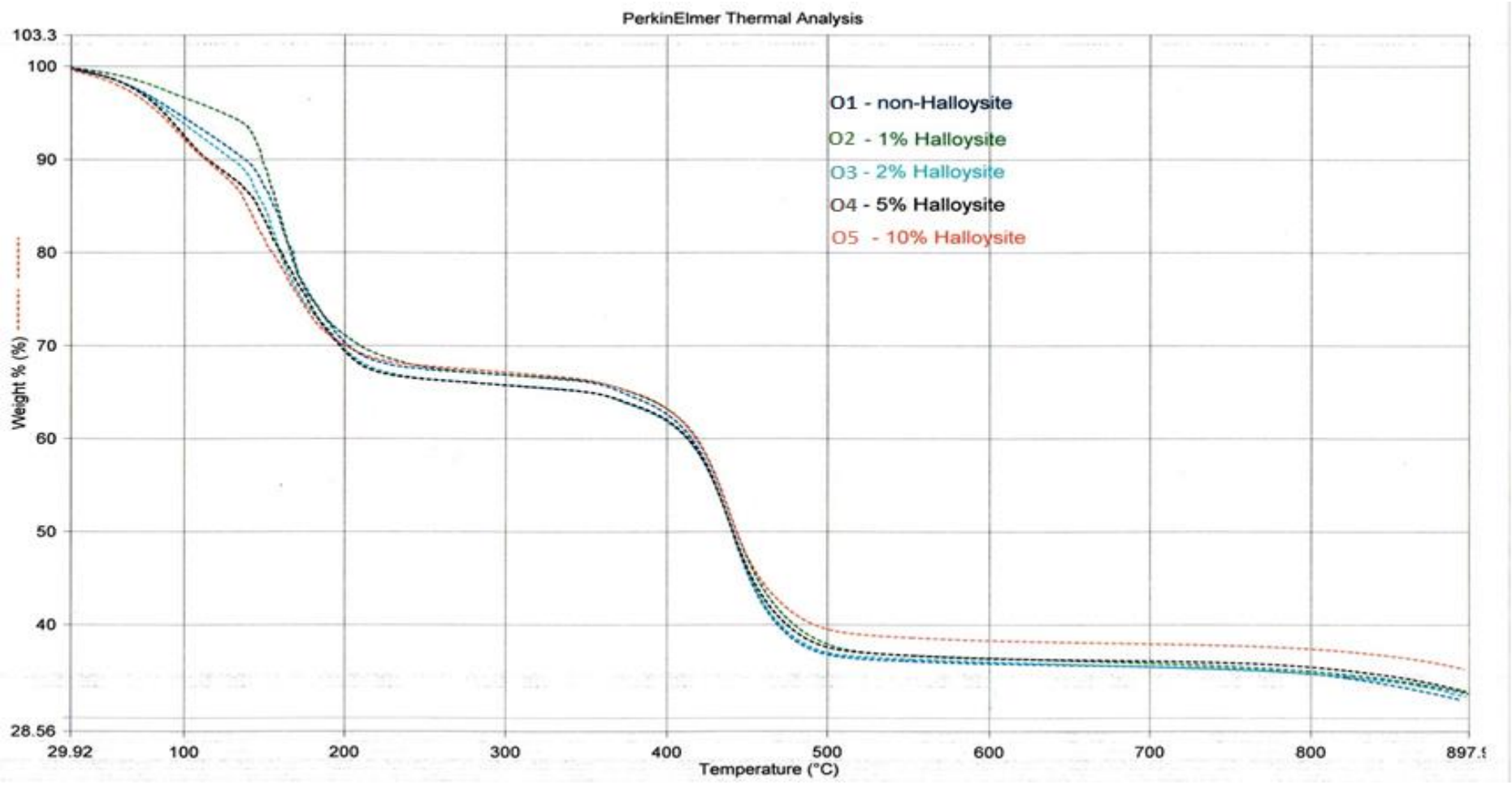


Figure 4.16 : Oven curing metal paints TGA results.

5. CONCLUSION

In this study, synthesized epoxy ester resin as the binder of two different curing paints has been reached the specification values that was determined prior to synthesis. According to tests for this epoxy ester resin it has shown low hardness, high gloss and gloss retention. Additionally it has shown good flexibility and good adhesion also high impact resistance.

Two different curing paints were designed to see the effect of halloysite on paint. These paints were mixed very well with halloysite at low speed in a short time. Then paints with halloysite additive were subjected to detailed tests.

According to viscosity and solid results of two different curing paints, viscosity increased very little with halloysite for oven curing paint. Solid results were reduced with halloysite for air drying paint. These effects can be easily tolerated by making small changes in the amount of given solvent. When looking at the results of density that has been seen with the increased amount of halloysite was decreased density of air drying paint whereas increased density of oven curing paint. Air drying paint included high amount of zinc which had high density, since the density of halloysite was quite less than that of zinc, air drying paint density was decreased with addition of halloysite. Two different curing paint coverage results were not changed with the addition of halloysite and there was not any negative effects. One of the most positive results of all these tests was gloss performance of halloysite which was fairly increased gloss of oven curing paint. There has not been a delay in the drying time of air drying paint with halloysite addition. Air drying paint had a high hardness because it contains quite high amounts of zinc this hardness after halloysite was added, has decreased in a significant way. Oven curing paint showed lower hardness rather than air drying paint because it contains less amount of inorganic filler raw materials and its hardness increased with the addition of halloysite.

Halloysite was envisaged as enhance the impact resistance of paints but all paints showed impact resistance at all heights. Thus impact resistance results did not show

this expected positive effect.

In the same way all paints had excellent flexibility due to this reason the effect of halloysite on flexibility could not be seen. Oven curing paint showed very good adhesion to all surfaces and halloysite has not reduced the adhesion. Air drying paint adhesion was relatively worse than oven curing paint especially on aluminum and galvanized surfaces. Halloysite has been observed to reduce adhesion of the air drying paint on the aluminum surface. It has been seen that air drying paint corrosion resistance higher than oven curing paint due to cathodic protection of zinc. Halloysite did not have any impact on the corrosion resistance of paints.

TGA analysis of halloysite added paints have shown very positive results. According to the analysis both different curing paints have experienced less mass loss and thermal resistance with halloysite. Otherwise halloysite added oven curing paints could maintain film structure after came out of the oven. As a result, it can be said that halloysite can be used as fire resistant additive in paints due to its thermal behavior.

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